Studies on Metallization of RP Parts for use in Preserving Artefacts

Thesis submitted in fulfillment of the requirements
for the award of the degree of

Master of Technology (Research)

in

Mechanical Engineering

Submitted by
Rameez Malik
(Roll No. 613ME1002)

Under the supervision of
Prof. SibaSankarMahapatra

Department of Mechanical Engineering
National Institute of Technology
Rourkela-769008, India

Dedicated to my family without whose efforts this could not have been possible

Department of Mechanical Engineering

National Institute of Technology Rourkela

December 29, 2015

Certificate of Examination

Roll Number: *613ME1002*

Name: *Rameez Malik*

Title of Dissertation: *Studies on Metallization of RP Parts for use in Preserving Artefacts*

We the below signed, after checking the dissertation mentioned above and the official record book (s) of the student, hereby state our approval of the dissertation submitted in partial fulfillment of the requirements of the degree of *Master of Technology (R)* in *Mechanical Engineering* at *National Institute of Technology Rourkela*. We are satisfied with the volume, quality, correctness, and originality of the work.

Sushanta Kumar Panigrahi
External Examiner

Siba Sankar Mahapatra
Principal Supervisor

Saurav Datta
Member, MSC

Bipin Bihari Verma
Member, MSC

R. K. Behera
Chairman,MSC

CERTIFICATE

This to certify that the thesis entitled —**Studies on Metallization of RP Parts for use in Preserving Artefacts** being submitted by **Rameez Malik** for the award of the degree of Master of Technology (Research) (Mechanical Engineering) of NIT Rourkela, is a record of bonafide research work carried out by him under our supervision and guidance. **Mr. Rameez Malik** has worked for more than two years on the above problem at the Department of Mechanical Engineering, National Institute of Technology, Rourkela and this has reached the standard fulfilling the requirements and the regulation relating to the degree. The contents of this thesis, in full or part, have not been submitted to any other university or institution for the award of any degree or diploma.

Dr. Siba Sankar Mahapatra
Professor and Head,
Department of Mechanical Engineering,
National Institute of Technology, Rourkela

Place: Rourkela
Date:

ACKNOWLEDGEMENT

This thesis is a result of research that has been carried out at **National Institute of Technology, Rourkela**. During this period, I came across with a great number of people whose contributions in various ways helped my field of research and they deserve a special thanks. It is a pleasure to convey my gratitude to all of them.

In the first place, I would like to express my deep sense of gratitude and indebtedness to my supervisor **Prof. S.S. Mahapatra** for his advice and guidance from the early stage of this research and providing me with extraordinary experiences throughout the work. Above all, he provided me unflinching encouragement and support in various ways which exceptionally inspire and enrich my growth as a student, a researcher and a scientist.

I specially acknowledge **Prof. S.S. Mahapatra** for his advice, supervision and crucial contribution as and when required during this research. His involvement with originality has triggered and nourished my intellectual maturity that will help me for a long time to come. I am proud to record that I had opportunity to work with an exceptionally experienced professor like him.

I am grateful to **Prof. S.K. Sarangi**, Director, **Prof. S.S. Mahapatra**, Head of Mechanical Engineering Department and **Prof. S. Datta,** Professor, Department of Mechanical Engineering **Prof. S.K. Patel**, Professor, Department of Mechanical Engineering, **Prof. S.K. Sahoo**, Professor, Department of Metallurgical and Materials Engineering, National Institute of Technology, Rourkela, for their kind support and concern regarding my academic requirements. I am very much thankful to all my teachers

I express my thankfulness to the faculty and staff members of the Mechanical Engineering Department for their continuous encouragement and suggestions. Among them, **Sri P. K. Pal** and **Sri Sambit Senapati** deserve special thanks for their kind cooperation in non-academic matters during the research work. I am also thankful to **Prof. S.K. Patel,** Professor, Department of Mechanical Engineering, for providing me the facility and guidance for performing the experiments.

I am indebted to **Dr. Saurav Dutta, Mr. Swayam Bikash Mishra, Mr. Suman Chatterjee, Mr. Kumar Abhishek, Ms. Bijaya Bijeta Nayak, Mr. Chhabi Ram Matawale, Mr. Manas Ranjan Singh, Mr. Rajiv Kumar Yadav, Mr. Chinmaya Prasad Mohanty, Mr. Kasinath Das Mahapatra, Mr. Mantra Prasad Satpathy, Ms.**

Shrutee Nigam, Mr. Ankit Pandey, Mr. Asutosh Pattnaik, Ms. Sanjita Jaipuria, Mr. Tijo D. and Mr. Arabinda Khuntia for their support and co-operation which is difficult to express in words. The time spent with them will remain in my memory for years to come.

Special thanks are also due to **Dr. B.B. Jha and Mr. Subhra Bajpai, I.M.M.T., Bhubaneswar,** for allowing me to use their research facility.

My parents and **my sister** deserve special mention for their inseparable support and prayers. They are the people who showed me the joy of intellectual pursuit ever since I was a child. I thank them for sincerely bringing me up with care and love. I thank them for being supportive and caring.

Last, but not the least, I thank the one above all of us, the omnipresent God, for giving me the strength during the course of this research work.

Rameez Malik

ABSTRACT

Properties like easy formability, light weight and corrosion resistance constitute natural advantage of plastic over metal. However, there are many areas in which metallic properties are required or demanded due to decorative or technological considerations. It is in these applications that the possibility of metallizing plastics has opened the door to new use for these materials. Metallization is a process in which a non-conductive material such as plastic is made conductive by providing a conductive layer on it. Due to this, possibility of utilizing the advantages of both metal and plastic in combination has been increased. As a result metallized plastic is widely used in fields like oil and gas, automotive industry, electronic industry, chemical processing, textile, aerospace, providing finishes on fashion items such as shoes, name badges, as well as on consumer electronics products including laptop cases and cell phones etc. Plastics such as polysulfone, polypropylene, polythene, teflon and acrylonitrile-butadiene-styrene (ABS) can be metalized with different metals like copper (Cu), zinc (Zn), nickel (Ni), gold (Au), chromium (Cr) and silver (Ag) using variety of processes like brushing a metal paint, spray metal technique, dipping in a metal paint, sputtering, electroplating, electroless plating and vacuum metallization. Among these processes, electroplating is widely used because of its simplicity and economy. In this method, metal ions in aqueous solutions are deposited on the activated plastic surface by an electro-chemical reaction with the aid of an electric potential, forming a thin metallic layer. In this work, possibility of metallization on RP parts through electroplating route has been explored for preserving artefacts.

Keywords: *ABS Plastic; Electroplating; Fused Deposition Modelling; Metallization; Rapid Prototyping*

Table of Contents

List of Figures

List of Tables

Glossary of Terms

Symbol	Full Form
.stl	Standard Tesselation Language
2D	Two Dimensional
3D	Three Dimensional
ABS	Acrylonitrile Butadiene Styrene
AC	Alternating Current
Adm^{-2}	Ampere per Decimetre square
AE	Acoustic Emission
ASTM	American Society for Testing of Materials
C	Carbon
$C_3H_3N_z$	Acrylonitrile
C_4H_6	Butadiene
C_8H_8	Styrene
CAD	Computer Aided Data
CAM	Computer Aided Manufacturing
CNC	Computerized Numeric Controlled
COF	Coefficient of Friction
Cr(VI)	Chromium
CrO_3	Chromium Trioxide
CRP	Controlled Radical Polymerization
Cu^{2+}	Copper ion
Cu_2O	Copper Oxide
$CuSO_4$	Copper Sulphate
DC	Direct Current
dm^{-2}	Decimetre square
DMA	Dynamic Mechanical Analysis
EDC	Electric Discharge Coating
FDM	Fused Deposition Modelling
$FeCl_3$	Ferric Chloride
Fig.	Figure
F_X	Force in X direction
F_Z	Force in Z direction
gL^{-1}	Gram per Litre
$H_2C_2O_4.H_2O$	Oxalic Acid
H_2O_2	Hydrogen Peroxide
H_2SO_4	Sulphuric Acid
HCHO	Formaldehyde
HCl	Hydrochloric Acid
HNO_3	Nitric Acid
J/m	Joule per Metre
LOM	Laminated Object Manufacturing

MLE	Multi Layered Electrode
mm	Millimetres
MnO_2	Manganese di Oxide
MPa	Mega Pascals
MTR	Metal Transfer Rate
N	Newton
NH_4F	Ammonium Fluoride
Ni	Nickel
^oC	Degree Centigrade
PC	Polycarbonate
Pd	Palladium
$PdCl_2$	Palladium Chloride
$PdSO_4$	Palladium Sulphate
PP	Polypropylene
PPy	Polypyrrole
PVD	Plasma Vapour Deposition
R_a	Roughness Average
RP	Rapid Prototyping
SEM	Scanning Electron Microscope
SGC	Solid Ground Curing
SLA	Stereolithography
SLS	Selective Laser Sintering
Sn	Stannous
$SnCl_2$	Stannous Chloride
Ti	Titanium
TiC	Titanium Carbide
TiN	Titanium Nitride
TWR	Tool Wear Rate
UV	Ultraviolet
V	Volt

Chapter 1

Introduction

1.1 Background

An artefact is an object reflecting human skill involvement, typically of cultural or historical interest. Artefacts generally provide us important knowledge about the past. Thus, they need to be handled with extreme care and should be preserved carefully. Artefact preservation is difficult because it is delicate and fragile and prone to weathering. As the skill level has been declined over the years, use of replicas instead of the original artefact has gained significant importance. The replicas are fabricated in such a way that they look exactly like the original artefact without any differences and are kept on display; thus eliminating risk factor.

The current methods of preserving artefacts by creating replicas are quite complex and need professional guidance. For example, for the manufacturing of a replica of a spearhead, a billet of smelted iron is used. The billet is then forged into the required shape and then chiseled. The socket is also forged from a piece of smelted iron and forge welded to the billet. The forging usually takes more than five hours and the grinding and finishing operations takes more than three hours. For finishing, a York stone is generally used. The whole process requires technical expertise and a lot of time to be completed. Hence, an alternate method has been suggested in this research work using Rapid Prototyping (RP) route which is much simpler. The accuracy obtained through RP is high and the time required is also less [1]. For preserving the replica, the prototyped part needs to be metallized so that it can be protected from wear and tear. The details as to how to use RP and its metallization process have been presented in the following sections.

1.2 Rapid Prototyping

Rapid prototyping (RP) is a collection of techniques that is used to quickly manufacture a scale model of a physical entity or assembly using three-dimensional computer aided design (CAD) data. Construction of the part or assembly is mostly done using three dimensional (3D) printing or "additive layer manufacturing" technology. A rapid prototyped part is shown in Figure 1.1.

Rapid Prototyping was first used in the late 1980s to produce models and prototype parts. Today, they are used for a wide range of applications for manufacturing quality parts in relatively small numbers if desired.

Figure 1.1. A Rapid Prototyped part

Similar to the Computerized Numeric Control (CNC) subtractive methods, the computer-aided-design - computer-aided manufacturing (CAD-CAM) workflow in the Rapid Prototyping process starts with the creation of geometric data as a 3D solid using a CAD workstation or two dimensional (2D) slices using a 3D scanner. The data must represent a valid geometry in which boundary surfaces enclose a finite volume, no holes are exposing the interior and the surfaces do not fold back on themselves. In other words, the object must have a distinct inside and outside surface. A model can be prototyped only if the computer can decide whether each point lies inside, on or outside the boundary surface of the model in a 3D space. After the complete CAD model is generated, it is converted into stereolithography format (.stl). This file format is the standard format for transferring solid geometric models to Small Form Factor (SFF) machines. A geometric model is sliced into layers as shown in Figure 1.2 to obtain the necessary motion control trajectories and these slices are then scanned into lines thus generating a 2D drawing as in a CNC's tool path.

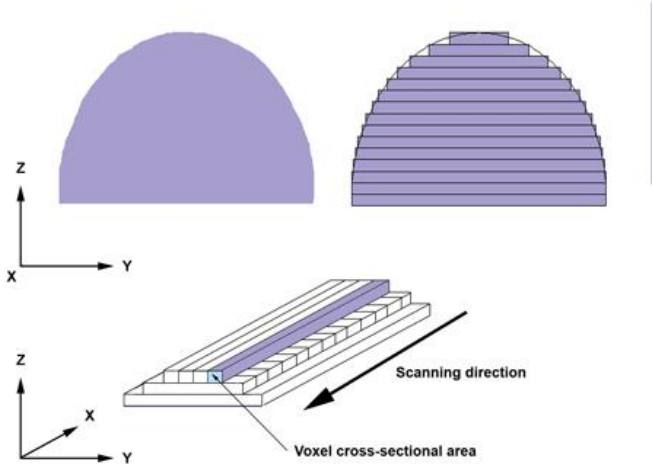


Figure 1.2. 3D Model Slicing

Additive manufacturing has following advantages compared to classical subtractive fabrication methods like milling, turning:

1. Objects of complicated geometry can be easily manufactured without the need of elaborate machine setups.
2. Rapid prototyping process is a relatively simple, straightforward and fast process.
3. Multiple parts of an assembly can be printed simultaneously. The support material can then be removed later.
4. Additive manufacturing makes the minimum amount of wastage which makes it a low cost and sustainable form of production.
5. Different types of materials can be used for different purposes.

1.3 Various types of rapid prototyping techniques

Some of the commonly used RP techniques are:

1.3.1 Stereolithography (SLA)

Stereolithography is a computer controlled technique for creating three dimensional objects. The process is based on the selective polymerization of a photosensitive resin using ultraviolet light. The ultraviolet light is focused on the top layer of the resin kept in a vat. The light is positioned and moved in X and Y directions to polymerize the resin within a particular boundary. The polymerized layer is lowered by the platform attached and a fresh layer of liquid resin is poured on it.

Advantages

- Accurate.
- Capable of high detailing.
- Good surface finish.

Limitations

- Post curing is required
- Shrinkage and curls might be present due to phase change
- Only photo polymers can be used

1.3.2 Selective Laser Sintering (SLS)

In this process, powdered material (usually metal) is spread on a layer. The powder is spread in accurate amount with the help of a counter rotating roller. A laser beam fuses the powder by scanning in a cross-section manner. The platform is then lowered

through a distance equal to the layer thickness and a new layer of powder is spread on the existing layer by the roller.

Advantages

- A variety of materials can be used.
- Build time is less.
- No post curing is required.

Limitations

- Surface finish is rough.
- Changing of materials is tough.
- The mechanical properties achieved are not upto the mark.

1.3.3 Fused Deposition Modelling (FDM)

In this process a thermoplastic material is melted and deposited selectively to form each layer of the part. The material used is in the form of a coiled wire which is mounted on the machine and is then melted and extruded with the help of the FDM head. The head moves in horizontal X and Y directions whereas the build platform moves in the vertical Z direction for producing each layer. After the completion of a layer the platform descends and another layer is built on top of the built layer.

Advantages

- Variety of materials can be used.
- Material changing is easy.
- Environment friendly.
- Economical machines.

Limitations

- The surface finish is not too smooth.
- Support material is required in some cases.
- Large parts take a lot of time to be fabricated.

1.3.4 Laminated Object Manufacturing (LOM)

Laminated Object Manufacturing came into existence because of Helisys Inc. In this process, the adhesive coated layers of the substrates are adhered to the platform with the help of a heated roller. A laser then traces the outline of the desired dimensions of the prototype through the layer of the material. The laser then cross-hatches the part of the material that does not form a part of the prototype to make the waste removal process easy. The build platform is then lowered by a distance equal to that of the

thickness of one layer and a new layer of material is rolled on the already built layer and the process is repeated. After the complete fabrication of the part, it is removed from the platform and the cross-hatched areas are broken away.

Advantages

- The process is speedy and cost effective.
- Handling of materials is easy.

Limitations

- Finishing quality is not very good.

1.3.5 Solid Ground Curing (SGC)

This process uses photo polymer resins and an ultraviolet light source. Based on the layer thickness and the geometric model the cross section of the slice layer is calculated. The platform is levelled and thereafter covered with a thin layer of the liquid polymer. The CAD data is utilized to create a mask which is placed above the surface of the resin and resin is exposed to the UV light source. After curing, the excess resin is removed and the voids are filled with molten wax. A cold plate is then used to solidify the liquid wax and the layer surface is then trimmed to the desired thickness. The built layer is then covered with a fresh layer of the resin and the process is repeated

Advantages

- No support structure is required.
- The model produced is accurate.

Limitations

- Waste production is high.
- The operation cost is high.

1.4 Metallization

Metallization is the process of coating non-metallic objects with metal. The need for metallization grew quickly with the introduction of plastics like Acrylonitrile Butadiene Styrene (ABS) as plastics are light weight and corrosion resistant and thus can be used in place of metals in many cases. But in certain applications, plastics need to be plated due to technical or decorative requirements. It is because of these requirements that metallization of plastics came into existence. Since plastics are poor conductors of electricity, the specimen’s surface first needs to be made conductive for subsequent metallization to take place. A metallic layer on a plastic part can increase its electrical conductivity and abrasion resistance and also give it a glossy appearance. Metalized

plastics are thus replacing plated metal parts due to their controlled electrical conductivity, low weight, ease of assembly and corrosion resistance. The variable metallization processes that are available these days are mentioned below.

1.5 Types of Metallization processes

A number of ways by which non-conductors can be metalized are discussed below.

1.5.1 Vacuum metallization

Also known as Physical Vapour Deposition or PVD, this technology is widely used to plate plastic parts with a thin aluminium layer. The outside as well as the inside of the part can be coated; however, in the latter case a plastic layer protects the metal coating. The deposition method is completely physical involving high-temperature vacuum evaporation followed by condensation. In order to obtain a glossy and reflective coating the specimen surface should be coated with a lacquer prior to the metallization process.

1.5.2 Electroless Plating

Electroless Plating refers to the process of metallizing non-conductive substrates without the use of electricity. The most frequently used metals for this type of deposition are nickel and copper. In this process, the specimen surface is first etched with a strong oxidizing agent which creates micro voids on the surface. This increase in the surface area makes the surface hydrophilic which helps in the bonding between the plastic surface and the deposited metal. After the completion of the etching process, the part is activated usually with the help of $PdCl_2$ and immersed in a solution and a metal coating is formed.

1.5.3 Electrolytic Plating

Electrolytic plating or electroplating is the process of depositing a metallic layer on a conductor with the help of an electric current. For metallization of a plastic, the plastic surface should be first made conductive by any method and then only can it be electroplated. The specimen to be electroplated is immersed in a solution of metal salts connected to a current source and acts as the cathode and another conductor made from the same metal as that of the metal salt is immersed in the bath which serves as the anode and thus the circuit is completed. Current flows from the cathode to the anode and the electrons flow in the opposite direction and are thus deposited in the cathodic workpiece.

1.5.4 Flame and Arc Spraying

These processes are low cost processes where a handheld or automatic gun is used to spray the liquid metal on the specimen. The metallic layer obtained is thick and the deposition rate is also high but the metal quality obtained is comparatively low. The coating is porous and the surface roughness is high relatively.

1.6 Need for Research

Preservation of artefacts has been a challenging task owing mainly to the deficiency of the availability of skilled workers. To overcome this problem an alternate method has been suggested involving the prototyping of artefact replicas via RP route followed by metallization of the same. Metallization of plastics started as early as 1940. But very little has been done to actually make good use of this process. Plastics like Acrylonitrile Butadiene Styrene (ABS) is one of the plastics that is metallized for various applications due to its high strength and good surface roughness values [2-4]. The controllable process parameters seem to change the quality of plating achieved but the extent of change has not been mentioned clearly [5-7]. The existing surface pre-treatment processes are quite complicated and expensive. As a result, the entire process becomes time consuming and costly [8-15]. Processes have been shown where the cost has been reduced but the complexity could not be dealt [16-29]. There are processes where metals can be deposited quickly without many complications but those processes are not suitable for plastics as they can only work with a conductor [30-38]. Even if the plastics are made conductive, still the processes do not work as the conductive layer is too thin to support those methods.

The following research gaps have been found out after an exhaustive literature survey:

- Very few studies have been carried out on the electroplating of plastics which is a much simpler method than electroless plating.
- For pre-treating the specimen surface, the methods suggested are too complicated and time consuming.
- The process to make the surface conductive, which is a primary step for subsequent electroplating has not been studied in detail. The suggested procedures are either too costly or too complicated.

- The impact of the process parameters of electroplating on the quality of plating achieved has not been mentioned.
- The adhesion of the plating to the substrate has been studied qualitatively and not quantitatively.

In the present study, the application of metallized plastic for the preservation of artefacts has been studied. RP models of some artefacts were fabricated and tried for electroplating. The need of surface pre-treatment for making the specimen conductive was also studied. Furthermore, the process of making the specimen conductive was tried to be simplified. The effect of the current parameters on the quality of plating achieved namely, surface roughness, particle size and adhesion strength was investigated. A quantitative method for checking the adhesion of the final metal layer to the specimen surface was investigated [39-41]. Finally, a finite element analysis was performed for studying the result of the adhesion test [42-44].

1.7 Research Objectives

The objectives of this study have been framed keeping in mind the preservation of artefacts. Since metallization of plastics has been suggested as an option, exhaustive literature survey has been conducted on the same. A number of research gaps have been found through the literature survey presented in Chapter 2. Literature suggests that metallization of plastic can help in the reduction of use of metals in various applications. This not only reduces the cost but is also very convenient as plastics are light weight compared to metals and the metallic properties like conductivity, etc. can also be achieved. This also makes the handling of the objects easier. Thus, to make the use of metallized plastic suitable in place of metals, a proper method of metallizing needed to be found out which is both, cost effective as well as easy to conduct than the current methodologies.

To this end, the following are the objectives of this research work:

- To find a cost effective and easy method to metallize plastic.
- To check the necessity of the existing pre-treatment processes required for metallization of non-conductors.
- To check if the controllable process parameters have any effect on the quality of plating achieved.

- To check the adhesion of the plating achieved, in a qualitative as well as a quantitative way.
- To develop a finite element based model for studying the result of the adhesion test.

1.8 Structure of the Thesis

Chapter 1: Introduction

This chapter acquaints us with the current trends in artefact preservation and suggests a new method. Technologies like rapid prototyping and metallization have been introduced. It also justifies the present research work and its needs.

Chapter 2: Critical Literature Review

This chapter provides us with the background information of the research work undertaken. It represents a summary of the knowledge already available in the relevant field. Finally, a substantial research gap is found out after studying the available literature so that the present study can be deemed more relevant.

Chapter 3: Sample preparation through RP route

This chapter gave an overview of the material (ABS) and the process of manufacturing the specimen through FDM technology. It points out the advantages of fused deposition modelling and its entire methodology in detail.

Chapter 4: Coating of samples

In this chapter, metallization of ABS plastic has been studied via electroplating, as this process is cost effective and simple. The three replicas of an original artefact manufactured are referred as specimens 1, 2 and 3. Specimen 1 has been pre-treated, made conductive and electroplated at 20 Adm^{-2}. For the pre-treatment process, the cleaned specimen was etched in concentrated sulphuric acid. It was then washed and dipped in $SnCl_2$ solution for about an hour. The $SnCl_2$ solution was a mixture of 1 gram $SnCl_2$ crystals, 20 ml conc. HCl and deionised water. The specimen was then taken out and washed again thoroughly and allowed to dry naturally. It was then painted with silver conductive ink to make it conductive and thereafter electroplated. Specimens 2 and 3 were not pre-treated but were made conductive by applying the silver ink and electroplated thereafter at current densities of 20 Adm^{-2} and 1 Adm^{-2} respectively. A

number of specimens have also been electroplated in varying current densities to observe the variation in the surface roughness of the coatings and the particle size of the deposited metal particles.

Chapter 5: Adhesion Test

In this chapter, the qualitative as well as the quantitative tests have been performed. Firstly, the Scotch Tape test was performed on specimens 1 and 2 to check if the pre-treatment processes performed had any significant changes on the coating adhesion. Secondly, the same test was performed on specimen 3 see if the current density had any role in the determination of coating adhesion. After these qualitative tests, an optimum current density was used to coat another specimen and the coating adhesion of that specimen was found out by the Scratch testing method.

Chapter 6: Results and Discussions

This chapter points out that when electroplating a non-conductor, pre-treatment processes prior to making the specimen conductive is not necessary and these processes do not play an important role in the determination of the adhesion strength of the coating. However, the electroplating current density can change the adhesion strength and it was found out that on increasing the current density the adhesion strength decreased and so did the surface roughness and particle size. On conducting the scratch adhesion test on the specimen the critical load was found out and a finite element analysis showed the stress and strain concentration zones.

Chapter 7: Conclusions

This chapter presents the brief summary of findings, major contribution to research work and future scope of the research.

1.9 Conclusion

The present chapter emphasizes on the preservation of artefacts suggesting a simple, quick and cost effective method. RP route has been chosen for fabricating the replicas which are further suggested to undergo metallization. Since only thermoplastics are used for RP technique, knowledge has been shed on the metallization process of plastics also. The main research objectives and the layout of the thesis have also been presented.

Chapter 2

Literature Review

2.1 Introduction

The current chapter highlights the advances and problems associated with the metallization of plastics. The major problem was to search for a cheap process that could be used to metallize a non-conducting materials. The coating deposited needed to be well adherent and smooth and the method had to be simple. Another challenge was to ease or completely overcome the necessity of the pre-treatment processes as they were complicated, time consuming and in some cases, very expensive. A list of the journal names and citations has been provided in Table 2.1. The majority of the citations are taken from peer-reviewed journals whose full text was available.

Table 2.1 List of Publications Cited

Publications	**Citations**
Applied Surface Science	2
CIRP Annals - Manufacturing Technology	1
Electrochimica Acta	1
International Conference on Energy & Environmental Systems	1
International Journal of Adhesion & Adhesives	2
International Journal of Advanced Manufacturing Technology	1
Journal of Applied Polymer Science	1
Journal of Manufacturing Processes	1
Journal of Material Processing Technology	5
Journal of Material Science	1
Journal of Metals, Materials and Minerals	4
Materials and Manufacturing Processes	2
Materials Letters	1
Metal Finishing l	1
Platinum Metals Review	1
Polymer Communications	1

Rapid Prototyping Journal	1
Solid Freeform Fabrication Symposium	1
Surface & Coatings Technology	5
Thin Solid Films	2
United States Patent Office	5
Wear	2
Wiley Publishers	2
Total	**44**

2.2 RP Material

As far as materials for FDM are considered, the materials must have a well-defined range of solidification and melting points. The coefficient of thermal expansion should be low as should be the viscosity and shrinkage. The materials should also be able to solidify within a short time period and the preferred solidification temperature is around 5-10^{o} below the softening point. As thermoplastics like ABS, polyphenylsulfone, Polycarbonate (PC) etc. satisfy these demands; hence they are considered as suitable FDM materials [1].

The testing of the fatigue strength of FDM rapid prototyped ABS parts was carried out by Lee et al. [2]. The ultimate stress for the ABS specimens was found out to be 50 to 80 % of the ABS wire data whereas that of the ABS plus specimens was much higher and in the range of 75 to 80 %. Galantucci et al. [3] tried to decrease the surface roughness of FDM prototyped parts by changing the process parameters. It was seen from their study that slice height and raster width were the most important parameters. On treating the specimens chemically with dimethyl ketone the surface roughness value improved and the proposed chemical treatment was economic, fast and easy to use. Vasudevrao et al. found out the process parameter settings for obtaining the minimum surface roughness of FDM built parts [4].

2.3 Pre-treatment and Plating process

Liebig suggested the electroplating of articles with copper and other metals for protection purpose [5]. Walker [6] invented a process of coating plastics materials such as cellulosic plastic materials, urea resin, hard rubber, synthetic resins or phenol

condensation products in an inexpensive way. He also gave a method of treating the surface of the above materials so that an adherent coating could be applied. Since plastic is a non-conductor, he suggested a new method to first make the specimen conductive followed by metallization. His method comprised of sandblasting the specimen's surface to make it rough and cleaning it and dipping it in stannous chloride solution to make it suitable for the metallization process, thereafter, removing it from the solution and thoroughly washing it. The specimen was then treated in a mixture of ammoniacal silver nitrate solution and a reducing solution so that an adherent metallized silver layer could be deposited on the surface which was further used as the conductive layer for subsequent electroplating.

Rode and Winkler [7] formulated a method for controlling the controlling density to optimum deposition conditions in an electroplating process for specimens whose surface area cannot be determined easily. Their method involved one controllable power supply unit which the help of which the optimum current density could be achieved. A new evaporation system for metalizing polymers was developed by Griehl et al. [8]. The metallized layers had a thickness of over 10 microns. The coating process developed was free of stress and has the provision to use different metals together or one by one without losing the vacuum. Thus, energy requirements were significantly reduced. The adhesion of the layers obtained was very high and the machining parameters could be changed for specific requirements. Bruyn et al. [9] studied some aspects of vacuum metallization of non-conductors from an industrial stand. Their study involved ABS, PC, polypropylene (PP) and a glass fibre/epoxy resin material. These materials were pre-treated using the common methods namely flame treatment, mechanical treatment, lacquer treatment, oxygen plasma and chemical treatment. After the pre-treatment processes, an aluminium layer of nominal thickness of 0.1 to 1 microns was deposited by magnetron sputtering. The adhesion strength of the metallic layer was examined by the cross-cut test and the falling-weight test. Adhesion on the ABS and PC specimens were the best irrespective of the pre-treatment method. In the case of no pre-treatment also the adhesion was found to be good.

Narcus et al. [10] found a method for bright electroless plating process. The plastic surface was first suitably pre-treated and a copper layer was deposited via electroless deposition to act as the under layer. A bright secondary electroless coating of the desired metal was then deposited which acted as the over layer, thus completely eliminating the need of an electroplating process which is usually required to achieve brightness. Krulik

[11] studied the importance of catalysts for electroless plating process. He suggested that during the plating process a very thin layer of tin (Sn)-palladium (Pd) catalyst should be applied on the dielectric surface which should be then followed by electroless plating of copper or nickel. The method suggested is very useful for printed circuit boards which are very prevalent nowadays.

Yen et al. [12] further investigated on electroless copper plating on ABS plastic. He dipped the washed ABS specimen in a $PdSO_4$ solution which omitted the sensitizing and activating processes. The Pd^{2+} ions coordinated on the surface of the etched ABS specimen. The ABS-Pd^{2+} complex was then reduced to Pd^0 atoms in an electroless copper bath containing a formaldehyde reducing agent. These Pd^0 atoms act as catalysts and help in the initiation of the deposition of copper metal n the specimen. The deposition rate is comparatively slow initially but after about ten minutes it rose to that of the conventional methods.

Considering the poor tendency of plastics to bond to other materials, A. Kruse [13] found out a way of pre-treatment required owing to the inert chemical structure of the plastics. He suggested for corona treatment, the low-pressure plasma process and the fluorination process and compared their results. The low temperature plasma process resulted in excellent adhesion strength and the stability of the treated surfaces could also be maintained for several days. The use of hypophosphite as a reducing agent in electroless copper plating was studied by Cheng et al. [14]. Conventional methods used formaldehyde (HCHO) as the reducing agent but they found that it could release harmful gases. Hence they suggested the use of hypophosphite instead of HCHO. But in the baths using hypophosphite the catalytic activation of metals decreased. Hence a catalyst was required for the electroless deposition to continue. The surface morphology of the copper deposition was measured by a scanning electron microscope (SEM) and it was found that coating was smoother in the hypophosphite bath than in the standard formaldehyde bath.

A direct method of copper plating on non-conducting substrates was suggested by Ono et al. [15]. ABS resin was used as the substrate and the method used was not a conventional palladium based system but a modified one containing copper ions and a reducing agent. The substrates were catalyzed by treating in a $PdCl_2/SnCl_2$ mixed catalyst solution (Controlled Radical Polymerization (CRP) Catalyst) and accelerated in the CRP accelerator containing Cu^{2+}. Further copper electroplating was performed

without the use of formaldehyde. In the initial stage of direct plating, Cu_2O particles are formed which act as the stepping stones.

Surface conditioning or etching of plastics before the metallization process was studied by Teixeira et al. [16]. The standard etching process involves the dipping of the ABS specimen in a sulphuric or chromic acid solution, but due to the presence of hexavalent chromium (Cr^{+6}) it is difficult to operate environmentally. Hence, they suggested the chemical conditioning of the ABS specimens with non-polluting solutions of H_2O_2, HNO_3 and H_2SO_4 as an alternative to Cr^{+6}/H_2SO_4. The solutions could be optimized to perform as well as the chromium based solutions in addition to giving an environment friendly method.

Ning et al. [17] further studied the process of direct copper plating on ABS plastic. They used the CrO_3/H_2SO_4 solution containing Pd^{2+} ions for etching the substrates. The substrates were then catalyzed by Pd/Sn colloids and accelerated in an alkaline solution containing copper ions. The Pd^{2+} ions reduced the surface roughness and enhanced the adsorption of the colloids. The formation of Cu_2O in the solution helped in the formation of metallic copper between the Pd particles. Yfantis et al. [18] suggested the use of conductive polymers or polypyrrole powder for protective coatings. They eliminated the use of chromium baths as well as palladium. The specimens were coated in situ with polypyrrole and the coating was conductive enough for further copper plating. A study on surface activation for electroless plating was carried out by Tang et al. [19]. They conducted an experiment by using a biopolymer (chitosan) to fix catalyst metal on the substrate. After the ABS specimen was dipped in the chitosan solution, it was dried and immersed in a palladium chloride solution for making it conductive. The specimen was then nickel coated by electroless plating. This new method enhanced the adhesion of the plating layer by chemical sorption instead of physical sorption in the conventional methods which involved sensitizing and activating the specimens. Inagaki et al. [20] suggested a new method of electroless copper plating on ABS plastic without the need of chromic acid etching as well as eliminating the use of palladium as a catalyst. They modified the nitrile groups of the specimen into carboxylic acid groups in an aqueous solution of sodium hydroxide without the chromic acid etching and palladium catalysis process. The hydrolysed specimens were then metallized using electroless copper plating. Instead of the palladium catalyst, a silver catalyst was used in the plating process. The adhesion strength achieved could perfectly sustain the scotch tape test.

A new method of making ABS plastic conductive was found out by Li et al. [21]. They coated aluminium-carbon black containing enamel pastes onto the plastic surface after cleaning the surface with soap and distilled water. After allowing it to dry overnight, copper was deposited on the specimen's surface by electroless method. The new method of coating showed sufficient adhesive strength when tested by the scotch tape test method. Ng et al. [22] investigated on the electroplating of poly(butylene) terephthalate-poly(ethylene) terephthalate blend. They found out that surface modification using sodium hydroxide pre-treatment and palladium helped in subsequent electroplating of copper. The adhesion of copper as determined by the scotch tape test depended on the surface roughness of the specimen and palladium content of the activating bath. Plastics with ester functional groups could be etched with an alkali for metallization. Dechasit et al. [23] developed a new method for electroless plating of ABS polymer without using tin and palladium. The specimens were first etched and activated with Ni ions. Sodium borohydride solution was used for the reduction of Ni ions. The specimen was then dipped in an electroless nickel bath which automatically deposited a Ni film on the substrate. The adhesion between the Ni film and the substrate was tested by the scotch tape method and was found out to be same as that which were plated using tin and palladium. A simple metallization technique for ABS has been suggested by Bazzaoui et al. [24]. They found out that without chromium and palladium, ABS could still be properly metallized. They immersed the specimen in a polypyrrole (PPy) solution and after about one hour $FeCl_3$ solution was slowly added. This PPy/ABS specimen acted as the cathode with copper as the anode for subsequent electroplating. The coating adhesion was then checked by the scotch tape test and was found to be satisfactory. A palladium free activation technique was found out by Shu et al. [25]. In this method, the specimens were pre-treated by the degreasing and swelling process. Then they were immersed in a solution of MnO_2-H_2SO_4 followed by neutralizing in a solution of $H_2C_2O_4.H_2O$. After the above processes, the ABS specimens were immersed in a solution of $CuSO_4$, by which Cu^{2+} ions were adsorbed on the ABS specimen surface. These adsorbed Cu^{2+} ions acted as catalytic sites for further electroless deposition.

An environment friendly surface pre-treatment method for ABS was suggested by Ma et al. [26]. They used an etching system comprising of MnO_2-H_3PO_4-H_2SO_4 colloid instead of the conventional chromic acid solution. A swelling system containing tetramethyl ammonium hydroxide and 1-Methyl-2-pyrrolidinone was used to investigate the surface

swelling of the resin. After the electroless plating, the adhesion strength was checked and found out to be 1.04KN m^{-1}.

Electroless copper plating on self-assembled monolayers of modified ABS substrate was studied by Xu et al. [27]. They plated different types of modified ABS and found that 6-(3-(triethoxysilyl)propylamino)-1,3,5-triazine-2,4-dithiol monosodium monolayer had the smoothest and most uniform plating. The plating adhesion was then checked by the scotch tape test method. Luo et al. [28] found out a palladium free process for surface activation of polycarbonate engineering plastic. In their study, the specimen was rubbed with four different grades of sandpaper and placed in an oven maintained at 110^{o}C. It was then placed in an alcoholic solution to dislodge the grease. Following that, the specimen was divided into two parts; the first part was placed in an aqueous solution of nitric acid, hydrogen peroxide and ammonium fluoride (NH_4F). The other was etched, sensitized and activated by $SnCl_2$ and $PdCl_2$. Both the specimens were then plated in the electroless method and the results were compared.

Equbal et al. [29] investigated on metallization of FDM built ABS part. They followed two different conditioning processes for two different specimens. Specimen 1 was etched using chromic acid and specimen 2 was etched using a solution of sulphuric acid and hydrogen peroxide. For activation purpose Pd/Sn colloid was used. After surface preparation, both the specimens were plated with copper by electroless method and the electrical performance of the parts was checked. Specimen 1 etched with chromic acid and plated in a sulphuric acid bath showed better electrical performance and copper deposition than specimen 2 even when the bath was same.

A study by Gangadhar et al. [30] showed that during an Electric Discharge Machining (EDM) process, metal transfer from the tool to the machined surface is also possible under certain conditions. This can be useful for surface modification under suitable process parameters. They also found that during electro discharge processing in a liquid dielectric medium, the transfer rate of the metal from the tool to the workpiece can be increased by using a powder compact tool instead of a complete solid tool because the inter-particle strength in the case of a powder compact tool is less than that of a forged tool, thus aiding in the easier transfer of metal from the tool to the workpiece through the dielectric medium. Wang et al. [31] described a method for surface modification by electrical discharge machining. They used an ordinary EDM machine tool and kerosene liquid and deposited a hard ceramic layer on the workpiece surface with a titanium compressed powder electrode. This process is known as electrical discharge coating

(EDC). The EDC begins with the electrode wear during EDM, and this worn electrode material reacts chemically with the carbon particle decomposed from kerosene and creates a hard carbide layer on the workpiece. This carbide layer becomes a hard ceramic layer of about 20 microns in thickness. Thus a TiC ceramic layer was created on the workpiece. On measuring the hardness of the ceramic layer, it was found out to be more than three times higher than that of the base material and thus could be widely used for the strengthening of cutting tools.

The use of powder metallurgy compacted electrodes for electrical discharge surface modification was investigated by Ho et al. [32]. They concluded that powder metallurgy compacted electrodes produced more alloying than conventional solid electrodes. If the polarity is changed to negative then the coating layer becomes more uniform. The hardness of the recast varied between 200-1100$HK_{0.025}$ compared to the bulk material of 365$HK_{0.025}$. The transfer percent of copper from the solid workpiece was around 29% as compared to the powder metallurgy's workpiece of 78%. Hsu et al. [33] found a new method of producing EDM electrodes using rapid prototyping. To make the electrode conductive they used electroless nickel plating followed by electroforming copper. The electrode was electroformed because the elctroless plating produced a layer of 25 microns which would easily break when current or heat would pass through it. Therefore, a layer of 1mm thickness was achieved by electroforming. In electroless plating, the substrate was thoroughly washed, etched and roughened. Thereafter it was sensitised and using $SnCl_2$ and $PdCl_2$ respectively followed by the plating process. The electroforming process included degreasing, neutralization and acid washing, surface activation, electroforming of copper, anti-oxidation of the surface and drying. The current densities for anode and cathode were 2 and 4 A/dm^2 respectively.

Producing EDM electrodes using rapid prototyping technology was further studied by Monzana et al. [34]. They casted an electrode made of ABS plastic using a mould made by RP. The mould was then made conducive by painting it with a silver paint with the help of a brush. It was further electroformed with copper having a thickness of 0.5 mm. The copper shell was then taken out and used as the electrode. Owing to its less thickness, it was first filled with a conductive filler material to enhance its rigidity and was then incorporated in the new shell holder tool of the EDM machine. The electrodes worked with the same process parameters as that of the conventional electrodes but the roughness achieved was slightly higher.

Hwang et al. [35] concluded from their studies that a multi-layered electrode (MLE) in electric discharge coating containing alternate layers of titanium and graphite with the same dimensions have better effect on the workpiece than the bulk type. The graphite layer of the MLE enhanced the concentration of carbon element locally which increased the combination of Ti and C to form TiC thus enhancing the surface hardness and decreasing the surface roughness of the coated layer. The effect of discharge parameters on electric discharge coating was studied by Chen et al. [36]. They used a Ti powder compact electrode in pure nitrogen gas and the workpiece was Al alloy. It was seen that the material deposition rate varied with a change in the discharge parameters. A minimum amount of electric energy is required for the formation of the pure titanium nitride film on the surface of the alloy. If the electric energy is increased beyond the optimum level then self-propagating synthesis reaction of Ti powder and nitrogen gas takes place which deteriorates the surface quality of the deposit and cavities are also formed. Eswara et al. [37] discussed about the various process parameters in the electric discharge coating process. They used a powder metallurgy compact electrode of tungsten and copper. They concluded that on increasing the compaction load, the metal transfer rate (MTR) and the tool wear rate (TWR) decreased. MTR and TWR increased on increasing the pulse-on time and so did the roughness. The deposited layer was harder than the base metal and a gradual increase in hardness from base to the top deposited layer was observed.

In the book written by Schlesinger et al. [38], a detailed description of the modern electroplating method for copper is described. The suggested tank voltages for refining copper was 0.2 V for the cathode and the anode current density was 1.6-2.2 Adm^{-2}. For the operating conditions, the temperature range was 32-43^{o}C and the cathode current density was kept at 16-22 A dm^{-2}. It was also found that small amounts of alkali metals and alkaline earth salts smoothened the copper deposits.

2.4 Adhesion Testing

Perry [39] investigated on the scratch adhesion testing of hard, well adherent and thin coatings. He found that since the onset of coating loss triggered an increase in the acoustic signal, hence, the combination of acoustic signal with the microscopic observations indicated whether the coating failure occurred in a cohesive or adhesive mode. He also pointed out that the critical load depended on the coating thickness as confirmed for steel substrates in which the critical load increases with an increase in the coating thickness and substrate hardness. Perry also confirmed that the shear modulus

had a big role on the critical load. As shear modulus gets high for different types of coatings the critical load decreases.

Steinmann et al. [40] studied the influence of intrinsic and extrinsic parameters on the scratch adhesion testing. They concluded the following:

- The length of change of load with distance should be 10 $Nmm^{-1}$and the radius of the diamond tip should be 200 microns so that the number of parameters influencing the critical load is minimized.
- Scratch test basically refers to the deformation of the coating-substrate assembly, which indirectly refers to the deformation of the substrate itself. Hence, the critical load increases with an increase in the substrate hardness and coating thickness.
- The critical load also depends on the friction between the coated surface and the tip. The more the friction the lesser will be the critical load.

Bull and Rickerby [41] concluded from their studies that the value of critical load decreases as friction between the coating and the indenter tip increases but since the widths of the scratch are almost same for all specimens and the internal stresses are expected to be similar, the difference in the friction value must be due to the differences in the adhesion of the coating with the indenter. For conducting the scratch adhesion test the specimen surface or the coating should be completely smooth.

2.5 Finite Element Modelling

The stress analysis for adhesive joints was studied by Goncalves et al. [42] using a finite element model. They approached the analysis in two ways: linear elastic and elasto-plastic materials' behaviour. In the linear elastic case, it was observed that the interfaces suffered much higher peak stresses than the middle of the adhesive layer. This explained why most of the failures occurred in the interfaces. In the elasto-plastic case, the normalized stresses at the interface decreased as the load increased. A finite element modelling of the scratch test was performed by Felder et al. [43] for its mechanical analysis. They studied the behaviour of elasto-plastic materials during a scratch test. They compared the shape ratio and scratch hardness with the results obtained in normal indentation and found out that the shape ratio of the numerical results was in good agreement with the original scratch experiments performed by others. Beres et al. [44] simulated a finite element modelling for a TiN coated titanium alloy substrate. They concluded that during a scratch test a tensile stress is produced behind the indenter and a compressive stress is produced ahead of the moving indenter. The traverse cracks

generated in scratch testing are initiated due to the tensile stress generation whereas the compressive stress generated result in coating buckling.

2.6 Conclusion

The present literature survey reveals that a detailed study on the metallization of plastics is needed. For better comprehension of the literature gap, the literature review is divided into four sections namely, RP material, pre-treatment and plating process, adhesion testing and finite element modelling. This chapter shows the various problems that arise during metallization of plastic, specially ABS. It gives a detailed study of the various types of pre-treatment processes that are carried out nowadays which include sensitizing, neutralizing, activating, etc. The chapter also sheds light on how the metal coating deposited on the specimen can be checked for adhesion and how we can validate that result with the help of finite element modelling.

The aim of the current research work is to close the gaps that have been identified in the literature review in a relatively easy method. The study proposes a method for metallizing ABS plastic in a cheap and easy way compared to those that are prevalent nowadays. An attempt has been made to investigate the differences that arise due to a change in the plating parameters. The research work also focuses on checking the quality of coating achieved and also its adhesion and validates the same using ANSYS.

Chapter 3
Sample Preparation through RP Route

3.1 Introduction

There are many RP techniques that are used these days as already explained in Chapter 1. Out of available options, FDM technology was used for this study because of the following advantages:

- It is cost effective as the cost required to make one part is relatively less.
- The machining time for the specimen preparation is very less ranging from minutes to hours.
- It has a high accuracy of upto 0.005 inch.
- Since it is a computer controlled method, hence it is quite easy to use.
- Almost any design that can be designed in a CAD application can be fabricated using the FDM technology.
- The specimens produced are very strong and waterproof.
- The scaling of the part is automatic and very accurate so as to fit the specimen inside the production space.

3.2 Material

The material used for the study was acrylonitrile butadiene styrene (ABS-M30) [1]. ABS is a thermoplastic copolymer whose chemical formula is $(C_8H_8)_x \cdot (C_4H_6)_y \cdot (C_3H_3N)_z$. It is made by the polymerization of acrylonitrile and styrene in the presence of polybutadiene. The monomers are shown in Figure 3.1.

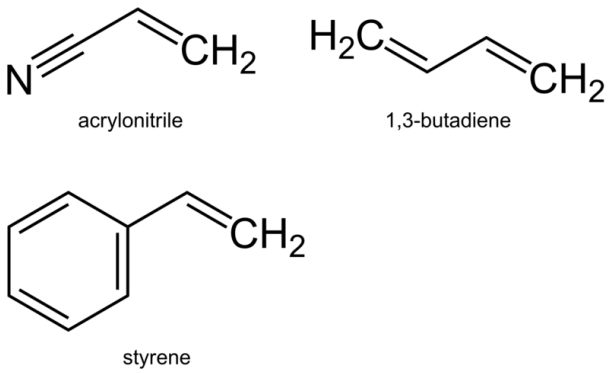


Figure 3.1. Monomers in ABS

The proportions of the monomers in ABS can vary from 40-60% styrene, 15-35% acrylonitrile and 5-30% butadiene. The composition may also contain wax (0-2%), mineral oil (0-2%) and tallow (0-2%). Acrylonitrile (chemical formula (CH_2CHCN)) is an organic compound and an important monomer for manufacturing plastics. It is

produced from propylene and ammonia. Butadiene is a synthetic rubber formed by the polymerization of 1, 3-butadiene. Styrene is a derivative of benzene and is a colourless oily liquid. In the polymerization of the above monomers, a long chain of criss-crossed polybutadiene is formed with shorter chains of poly(styrene-co-acrylonitrile). ABS is stronger than pure polystyrene because of the nitrile groups in the neighbouring chains which attract each other and bind the chains together. The three monomers in ABS provide a balance of properties with the acrylonitrile monomer providing heat resistance, butadiene imparting good impact strength and styrene providing rigidity to the copolymer. The properties of ABS-M30 are shown in Tables 3.1 and 3.2

Table 3.1 Mechanical Properties of ABS-M30

Properties	**Test Method**	**Value**	**Unit**
Tensile Strength, Yield	ASTM D638	26-31	MPa
Tensile Strength, Ultimate	ASTM D638	28-32	MPa
Tensile Modulus	ASTM D638	2180-2230	MPa
Flexural Strength	ASTM D790	48-60	MPa
Flexural Modulus	ASTM D790	1760-2060	MPa
IZOD Impact, notched	ASTM D256 2	128	J/m
IZOD Impact, unnotched	ASTM D256 2	300	J/m

Table 3.2 Thermal Properties of ABS-M30

Properties	**Test Method**	**Value**
Heat Deflection Temperature	ASTM D648	82^{o}C
Glass Transition Temperature	DMA	108°C
Coefficient of Thermal Expansion	ASTM E831	8.82x10-05 mm/mm/°C

3.3 Specimen Fabrication

The specimens are fabricated with the help of FORTUS 400 mc machine which used FDM technology. The machine, shown in Figure 3.2, is designed, developed and marketed by Stratasys Inc., 7665 Commerce Way, Eden Prairie, MN 55344, U.S.A. In comparison to the other machines like FORTUS 250mc, 260mc and 360mc, the 400mc provides a larger build chamber (355x254x254 mm). It can use a variety of build materials like ABSi, ABS-M30, ABS-M30i and Polycarbonate (PC). It uses a soluble support material for the ABS based materials and a breakaway support material for PC. Even though the support material is soluble for ABS, it can still be broken away by hand if the size is small. The parts can be built in four different layer thicknesses which are 0.33 mm, 0.254mm, 0.178mm and 0.127mm. The machine has two auto load model material and support material canisters with 14912223 cubic mm of material in each of the four canisters.

Figure 3.2 FORTUS 400 mc

For the fabrication of the artefact prototypes, a real artefact was used which is shown in Figure 3.3.

Figure 3.3. Artefact scanned to manufacture the specimens

The artefact was cleaned properly with a dry cloth and was then scanned. A 3D scanner FaroArm 7 axis Fusion manufactured by FARO Technologies Inc., U.S.A. was used for this purpose which can scan 3D real objects and convert the scanned image to a .stl file format. The machine has a 7-axis availability with infinite rotation for nonstop measuring. There are temperature sensors for higher precision and if the machine is idle for a prolonged period of time then there is an auto sleep mode to help save electricity. The 3D scanner used has been shown in Figure 3.4.

Figure 3.4. FaroArm 3D scanner

However, these prototypes could not be tested for adhesion and surface roughness values as those tests require a flat surface. Hence, cubic shaped specimens were made using CATIA V5. The CAD data was then exported in a .stl file format to Insight 8.0, the FDM software required to run FORTUS 400mc. Here, the STL model was broken into individual slices by the software and the tool path was generated. After the generation of the tool path, the data is sent to the machine for modelling. Six process parameters govern the fabrication of the specimens. They are:

Contour number: the number of outer layers in the specimen.

Layer thickness: the thickness of each layer.

Raster width: the width of each raster.

Orientation: the angle at which the specimen is fabricated with respect to the build platform.

Raster angle: the angle of each raster with respect to its previous one.

Air gap: the gap between two neighbouring rasters.

The parameters were set in such a way that the surface roughness of each specimen was minimum [3-4]. The parameter settings are:

Contour Number=1, Layer thickness=0.178 mm, Raster width=0.4064 mm, Orientation=0^o, Raster angle=0^o, Air gap=0 mm.

The modelling material (ABS-M30) is supplied in the form of a solid spool from a canister to the head of the machine. A schematic of the working process of FDM is shown in Figure 3.5. A pair of rollers having a small gap in between is used to grip the model material and advance it to the liquefier head. The liquefier head generates a temperature greater than the solidification temperature of the material and the material

is extruded in a semi molten state onto the build platform following the generated tool path. A picture of the liquefier head is shown in Figure 3.6. The head is supported by a gantry and connected to servo motors which maneuver the head in X and Y directions while building the part. The gantry supporting the head is located under the top hood of the machine and outside the build chamber. Only the tip of the extrusion nozzle is placed inside the build chamber. The build platform has the ability to move along the Z direction. The drive motions are so provided to move the extrusion head and the build platform relative to each other through the drive signals input to the servo motors from the CAD system. The FDM machine uses two separate nozzles for the deposition of the materials, one for the model material and one for the support material. The process is so designed that only one of the nozzles works at a time. For the generation of each layer, a contour is initially extruded to define the boundary layer or part boundary and the interior of the contour is filled thereafter through vector filling (known as raster). The raster angle is set to 90 degrees alternatively between the consecutive layers so that adequate interlocking can be obtained between the layers. The bonding of the fibres throughout the specimen occurs due to diffusion of the rasters during the solidification of the semi molten layers. A complete pictorial description of the steps involved during the specimen manufacture is shown in Figure 3.7.

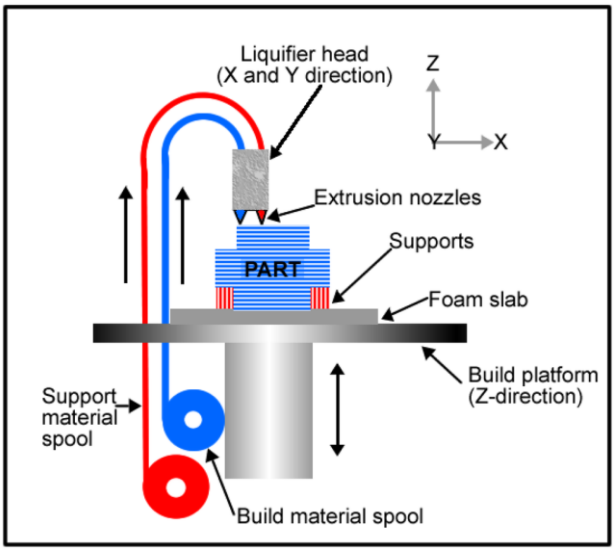


Figure 3.5. Schematic of FDM process

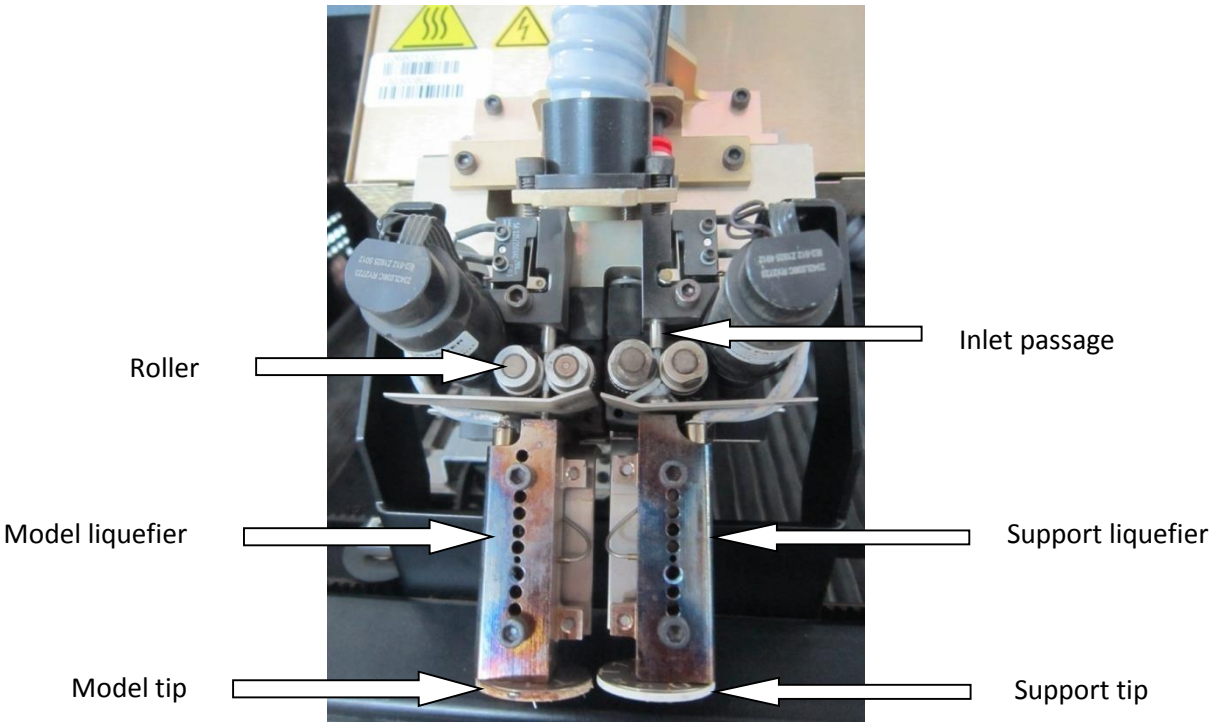
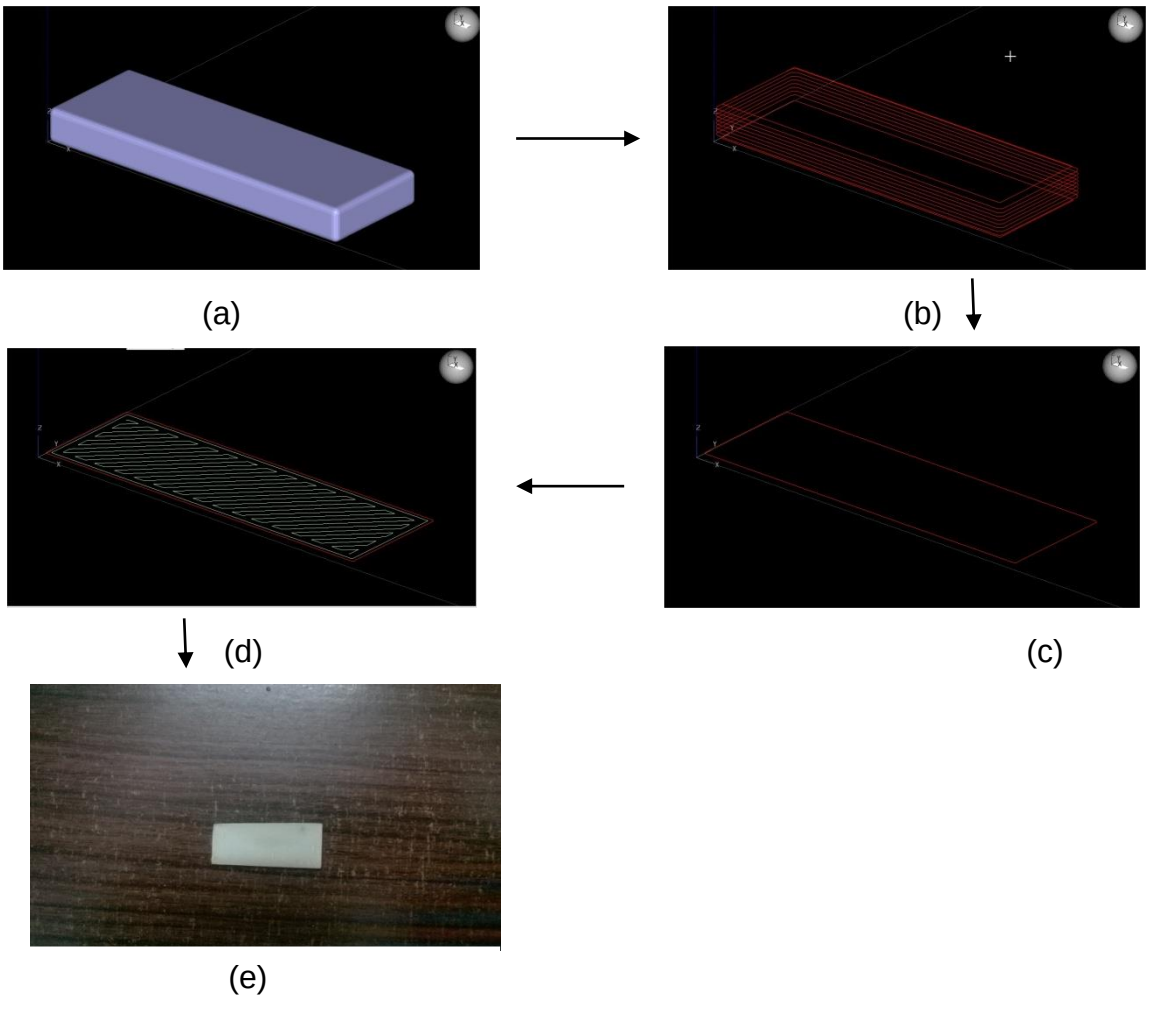


Figure 3.6. The liquefier head assembly



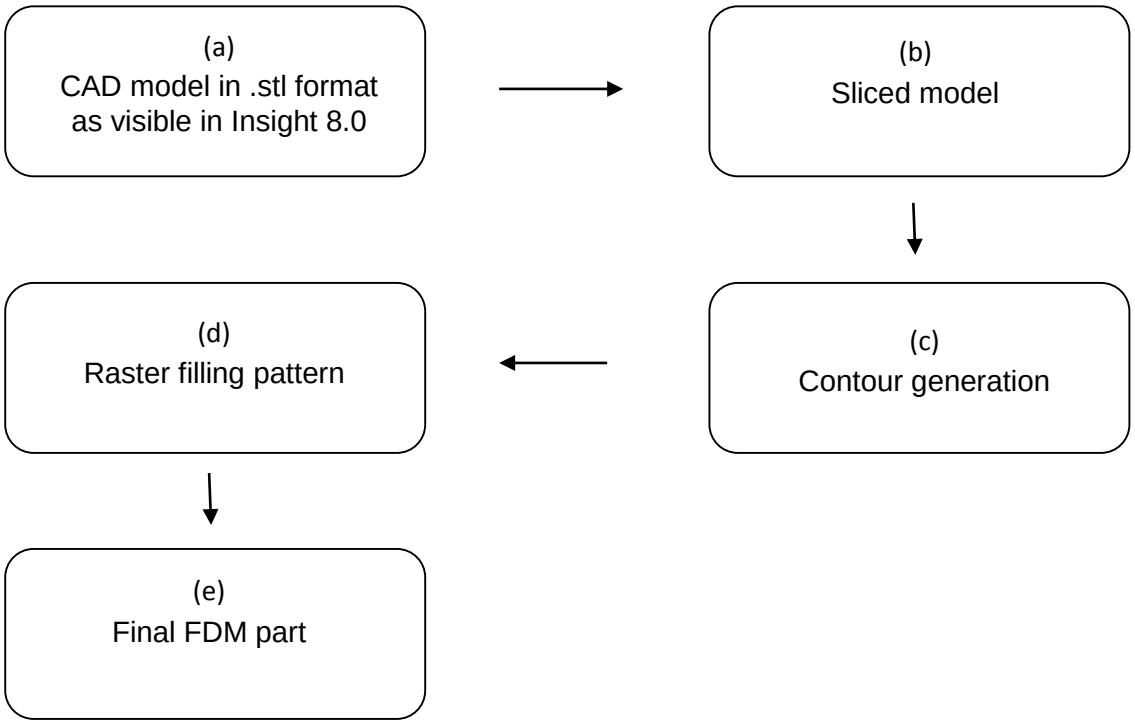


Figure 3.7. Steps involved in part fabrication

3.4 Conclusion

This chapter gave an overview of the material and the process of manufacturing the specimen through FDM technology. The following chapter presents the coating method undertaken to coat the specimen.

Chapter 4
Coating of Samples

4.1 Introduction

As already stated, the coating of a non-metallic object with a metal is known as metallization. Coating is usually done to improve certain characteristics of the substrate so that it can be used for various other applications like increasing conductivity, corrosion resistance, for aesthetic purposes, etc.

In this research, a number of coating processes have been studied that can be used to metallize ABS plastic and the most feasible of all i.e. electroplating, has been chosen keeping in mind the cost and complexity of the process. The substrates have been electroplated with and without pre-treatment processes to study the differences in the adhesion of the coatings. A number of substrates have also been electroplated in varying current densities to see the variation in the surface roughness of the coatings.

4.2 Pre-treatment

Pre-treatment process is one of the determining steps for the deposition of metal particles. The pre-treatment process is usually done to activate the polymer so that it can be made conductive easily for subsequent metallization.

After the FDM part has been built completely, the support material is normally broken away by hand. If the support part becomes too hard then the whole specimen is dipped in an ultrasonic cleaning tank. This cleaning tank manufactured by Supersonic, has an in-built heater and transducers. These transducers vibrate at ultrasonic frequencies resulting in the creation of minute bubbles which reach all surfaces immersed in the solution. This implosion of the bubbles safely removes the support material without affecting the ABS part. The ultrasonic frequency determines the size of the cavitation bubbles. Higher frequencies generate smaller and gentler bubbles capable of penetrating even small openings and are hence used for complex parts. Lower frequencies generate larger bubbles suitable for simpler parts and produce a vigorous cleaning. After the removal of the support material, the substrate was thoroughly washed and dried. Care was taken so that the substrate does not come in contact with any impurities. The FDM part produced had a very smooth surface but for the deposition of the metal ions the surface needed to be made rough [8-14]. For this purpose, the entire substrate was polished with grade 400 sandpaper. Polishing the surface made the surface rough which increased the surface area of the specimen for metal ions to deposit. Three specimens were manufactured for identifying the needs of the pre-treatment method which were then referred as specimens 1, 2 and 3. Specimen 1 was pre-treated whereas specimens 2 and 3 were not pre-treated.

Specimen 1 was etched with conc. H_2SO_4 by dipping it in the acidic solution [8, 10, 14-15, 17, 21, 23, 24, 26]. It was then washed thoroughly. Since ABS polymer does not react with many chemicals, hence the specimen needed to be sensitized and activated [11, 13-15]. For sensitizing, 1 gram of $SnCl_2$ crystals was added to 20 ml of conc. HCl. White crystals were formed during this process and deionized water was added in the solution until the crystals disappeared. Specimen 1 was then completely immersed in this solution for about an hour without any disturbance. After an hour it was taken out and washed thoroughly so that no amount of Sn was left on the surface. It was then washed and allowed to dry naturally at room temperature for a day. After drying completely the specimen was painted with a silver conductive ink which adhered to the plastic surface. This step was followed in the case of all the three specimens in a similar method. The main significance of this step was to make the specimens conductive. A standard paint brush of size zero was used for this purpose. The size of the paintbrush was chosen to be small so that the ink could be applied to every part of the specimen including the small and the complex zones. After painting the specimen, it was allowed to dry at room temperature. The specimen took around 15-20 minutes to become completely conductive. A multimeter was used to check whether all the surfaces of the specimen had become conductive or not. A pre-treated specimen is shown in Figure 4.1

Figure 4.1. A Specimen after pre-treatment

4.3 Electroplating

Electroplating is a metallization process which requires electric current to coat the substrate. An electroplating kit necessarily comprises of a dc current source, electrolyte solution, cathode, anode and beaker or container to hold the solution. In electroplating, the workpiece is connected to the cathode and the coating source to the anode. Both the cathode and the anode are connected to the power source and the circuit gets completed by dipping both in the electrolyte solution. When the circuit is

switched on electric current flows through it. The cathode being negatively charged attracts the positive ions from the anode and these ions deposit on the cathode and the process continues. The voltage required for plating was quite less. Even with high cathode current densities of 22 Adm^{-2}, a 10V current is sufficient if the solution is properly agitated. Current densities as high as 260 Adm^{-2} have also been reported to be used with vigorous agitation. The operating conditions for electroplating are very standard. The room temperature may vary from 18 to 60^{o}C, however, a temperature range of 32 to 43^{o}C is more common as it can be achieved with little or no cooling or heating. Plating bright copper in acidic solutions should be done at a temperature below 30^{o}C with constant agitation. An increase in the current density in the electrolyte solution tends to increase the cathode polarization. To nullify the effect of increased current density the solution should be suitably agitated. Hence, the agitation and current density must be balanced to achieve coatings with the desired properties. Generally current densities of 16-22 Adm^{-2} are used when the electrolyte is agitated with air. Long, fast moving wires can be plated at current densities as high as 50 Adm^{-2}. However, if the continuous movement of the workpiece is not possible or air agitation cannot be supplied, the optimum current densities are reduced to as low as 3.7-5.4 Adm^{-2} [35].

In this study, copper sulphate pentahydrate crystals were used to make the electrolyte solution. The concentration of the crystals in a conventional solution is kept around 200-250 gL^{-1} [35]. Copper sulphate crystals were dissolved in water to get the electrolyte solution accompanied by constant stirring. The solution obtained was fully saturated and royal blue in colour. Pure copper strips manufactured by Ottokemi, Mumbai, were used as anodes. The silver painted specimens were connected to the cathode. The specimens had to be used within one hour from coating with silver as otherwise the silver would have oxidized and the specimens would have lost their conductivity. An instrument capable of controlling the voltage as well as the current was used for converting the AC current to DC. The advantage of this instrument was that we could electroplate the specimens in our choice of current or voltage. All the three specimens were plated in the same procedure. However, the major controlling parameter in our case was the current density. To study whether there was any difference between the pre-treated and the untreated specimens, specimens 1 and 2 were electroplated at a current density of 20 Adm^{-2}. An electroplated specimen is shown in Figure 4.2

Figure 4.2. Specimen after being electroplated

After the plating process, both the specimens were tested for their coating adhesion by the X-cut method of the Scotch Tape test as described in the next chapter. The other untreated specimen (specimen 3) was electroplated at a current density of 1 Adm^{-2} for comparing the adhesion of the coatings achieved at different current densities. The plating parameters for the three specimens are shown in Table 4.1.

Table 4.1 Plating parameters for the three specimens

Specimen No.	**Total Surface Area (mm^2)**	**Pretreated**	**Current Density (Adm^{-2})**	**Voltage (V)**	**Time (mins)**
Specimen 1	4510	Yes	20	10	130
Specimen 2	4510	No	20	9	131
Specimen 3	4510	No	1	1	85

This specimen too was then tested for the coating adhesion by the same method. The result of the adhesion test clearly showed whether the pre-treatment process was a necessary step or not. However, it was observed that the surface roughness of specimen 3 was much higher than the rest. Hence, to find the dependency of surface roughness with current density, ten cuboid specimens of dimensions 30mm x 10mm x 3mm were fabricated using the same principle. These specimens were polished with sandpaper before plating. After polishing, the specimens were directly electroplated omitting the pre-treatment process because of the results achieved in the Scotch Tape test. The plating parameters used for plating these specimens were different from each other and depended on their surface areas as shown in Table 4.2.

Table 4.2 Plating parameters used for the ten specimens

Specimen No.	Total Surface Area (mm^2)	Current Density (Adm^{-2})	Voltage (V)	Time (mins)
4.	1203.30	1	0.8	63
5.	1178.51	2	1.5	59
6.	1151.51	3	2.5	54
7.	1398.24	4	3.7	48
8.	1107.20	5	3.6	45
9.	1264.58	6	5.2	38
10.	1361.07	7	6.5	30
11.	1250.97	8	6.8	23
12.	1165.35	9	7.3	17
13.	1332.20	10	8.1	11

The optimum current density for electroplating lies in the range of 3.5-5.5 Adm^{-2} [38]. Hence, the range of 1 to 10 was chosen accordingly to study the differences arising in the optimum current densities and its nearby values. The range was not increased beyond 10 Adm^{-2} because the coating adhesion decreased on increasing the current density as found out in the scotch tape test. The difference in the surface area is mainly due to the effects of polishing and hence while calculating the current density this was taken into consideration. To find out the difference in the coating properties due to the difference in plating current density, the surface roughness of all the specimens were found. After calculating the surface roughness, a specimen was sent for scratch adhesion testing of the coating. As opposed to the scotch tape test, this is a quantitative method of finding out the coating adhesion.

4.4 Conclusion

The present chapter explains the overall metallization process in detail. Light has been shed on the pre-treatment processes that are prevalent for metallizing ABS plastic. A comparative study has been conducted on three specimens for finding out the relation of the coating adhesion and the current density as well as to find out whether the pre-treatment processes are actually required or not. Scotch Tape test was conducted for qualitative analysis of the coating adhesion which showed that pre-treatment methods did not aide in the adhesion but current density played an important

factor. Since the test was only qualitative, more specimens were coated, their surface roughness calculated and the optimum was sent for scratch adhesion testing. Both these adhesion testing methods will be described in detail in the next chapter. Thus, a metallizing process has been found out which is both, cost effective and simple to perform. A simple and cheap method has been suggested to make the specimens conductive rather than going for the conventional methods. The need for pre-treatment processes has been completely eliminated and the effect of current density on the surface roughness has also been observed.

Chapter 5
Adhesion Test

5.1 Introduction

For any type of coating to perform satisfactorily, it must properly adhere to the substrate. There are many methods that can be used to examine the adhesion of coatings in both qualitative and quantitative manner. Qualitative tests like the ASTM D3359 determine whether the coating adhesion is good or bad i.e. it does not give any numerical value of the adhesion but still can be relied on. Quantitative tests like the Scratch test give us the exact numerical value of the coating adhesion i.e. the load at which the coating adhesion starts to fail. Hence, these tests are more preferred over the qualitative tests as they give a more accurate result. But the quantitative tests are difficult to perform. They require a completely different instrumental setup and laboratory conditions as well as high precision. That is why, if very accurate results are not desired, qualitative tests fulfill the purpose. After conducting the test, it should be noted whether the bond failure was adhesive (failure at the interface of the coating and substrate) or cohesive (failure within the coating film).

In this study the qualitative as well as the quantitative tests have been performed. Firstly, the Scotch Tape test was performed on specimens 1 and 2 to check if the pre-treatment processes performed had any significant changes on the coating adhesion. Secondly, the same test was performed on specimen 3 to see if the current density had any role in the determination of coating adhesion. After these qualitative tests, scratch testing was conducted on another specimen to find the critical load.

5.2 The Scotch Tape test

This test method is a procedure to assess the adhesion of coating films over a substrate by making cuts in the film and applying and removing pressure-sensitive tapes over the cuts. It determines whether the coating adhesion is at a generally adequate level or not i.e. it examines the coating in a qualitative manner. This method is not suitable for multiple coatings as the failure might occur between the coats and the adhesion of the coating to the substrate will not be determined. There are two methods of performing the Scotch Tape test:

Method A: An X cut is made on the film of the specimen. Pressure sensitive tape is applied on the cuts and removed and the adhesion is measured on a scale of 0 to 5.

Method B: A pattern of vertical and horizontal cuts of either 6 or 11 cuts is made in each direction on the film to the substrate. The pressure sensitive tape is applied on the pattern and removed, and the adhesion is measured by comparing the pattern with descriptions and illustrations.

Since method B can only be used for very thin coatings (less than 125 microns), hence, for our study method A was selected. Moreover, method B was difficult to perform on a curved surface. The details of method A are given in detail in the following section.

Test Method A- X cut Tape test

I. Apparatus

- Cutting tool- a knife, razor blade or any cutting device with sharp edges and in a good condition.
- Cutting guide- steel ruler or any hard metal straightedge to make straight cuts.
- Tape- a one inch (25mm) wide, semi-transparent tape with standard adhesion strength. If the tests are to be performed in different laboratories or in different times, a tape from the same batch should be used as the adhesion strength of the tape might differ from batch to batch.
- Rubber eraser- a rubber eraser on the end of a pencil.
- Illumination- a bright light source is required to help in determining whether the cut has been made through the film to the substrate or not.

II. Test Specimen

- The test specimen used was the original specimen on which the adhesion was to be evaluated. There was no need of making a specimen with ASTM size standards.

III. Procedure

- After the specimens were electroplated, they were allowed to dry properly and then cleaned.
- An area free of surface imperfections and blemishes was chosen as the testing area. The test was conducted in room temperature as an increase or decrease in the temperature and humidity could affect the adhesion of the tape.
- Two small cuts not longer than 40 mm were made on the testing area. The cuts intersected in their middle subtending a smaller angle of 30^{o}-45^{o} in the centre. The steel ruler was used as the guide while making the cuts and the cuts were made in one steady motion.
- The light source was used to inspect the cuts and check whether they had completely penetrated the coating film.
- If the cuts do not reach the substrate then a separate set of cuts should be made in a different location. Deepening a previous cut is not encouraged as this can affect the adhesion of the film along the incision.

- While applying the tape, two complete laps from the roll were removed and discarded. An additional length of 75 mm was removed in a steady motion (not jerked).
- The centre of the tape was placed at the intersection of the incisions along the direction of the smaller angles. The tape was then smoothened by finger on the area of the cut and then rubbed firmly with the pencil eraser so that it stuck properly at the point of the intersection. Since the tape was semi-transparent the colour under it helped to know when a good contact had been made.
- After around 60 to 90 seconds of application, the tape was removed by holding the free end and pulling it off in one rapid motion (not jerked) back upon itself almost at an angle of 180^{o}.
- The cut area was then inspected for coating removal and the adhesion was designated according to the following scale as shown in Table 5.1:

Table 5.1 ASTM designation scale of X-Cut Tape test

Designation	**Amount of coating removed**
5A	No peeling or removal
4A	Trace peeling or removal along incisions or at their intersection
3A	Jagged removal along incisions upto 1.6 mm on either side
2A	Jagged removal along most of incisions upto 3.2 mm on either side
1A	Removal from most of the area of the X under the tape
0A	Removal beyond the area of X

Based on the results of the Scotch Tape test, specimen 3 which was metallized at a current density of 1 Adm^{-2} was designated as 5A whereas specimens 1 and 2 were designated as 0A and 1A, both of which were metallized at a current density of 20 Adm^{-2} with and without the pre-treatment processes respectively.

5.3 Scratch Adhesion Test

Metallization of metals and non-metals have gained significant importance owing to their large number of applications in various industries like automobile, biomedical,

optical, etc. Since these coated substrates perform in an industrial environment, it is important for them to not fail in the middle of an ongoing job as this can be a hindrance to all the successive line up. Hence, it is of extreme importance that the quality of the coatings being used be checked thoroughly not only in a qualitative manner but also in a quantitative way [39-41]. The most important parameter to be checked is usually the adhesion of the coating and in some cases the surface roughness is also evaluated although it is not of primary importance. For checking the coating adhesion, two methods can be used for quantitative purposes namely the shockwave test and the scratch test (ASTM G171).

The shockwave test is a reliable and powerful method of checking the coating adhesion at the coating-substrate interface. A compression wave is generated in the specimen which then travels normally to the surface. As soon as the wave gets reflected at the surface, it changes into a tensile wave. If the adhesion is less than the peak stress value of the generated wave then there is a failure of the coating when the wave travels in the interface. The ratio of the coating thickness to the wavelength should be kept in mind; which must be greater than 2 else the wave would not be able to achieve its maximum tensile stress at the interface. However, in reality, the wave propagation is very complex and it is not actually possible to calculate the amplitude of the reflected wave as a result of which the adhesion cannot be determined. Hence, scratch testing is the only feasible option for this purpose.

The scratch test is a completely different process from the above. In this process the specimen is firmly held at one place and a stylus is made to traverse on the coated surface of the specimen. The specimen should be flat and small. The stylus is loaded either progressively or at once depending upon the adhesion to be checked. As soon as the coating is peeled off cleanly from the substrate the stylus is stopped. The load at which the coating starts to peel off is known as the critical load.

The machine used for the scratch testing was Brucker®-CETR® UMT scratch tester shown in Figure 5.1.

Figure 5.1 Scratch testing machine

The detailed process of the test is described below:

I. Apparatus

- Stylus and stylus mounting- the stylus present was a Rockwell-C spherical indenter of diameter 200 microns. The use of this type of stylus is emphasized so that the tests can be compared and reproduced between other laboratories.
- Stage- the mounting platform was so designed that it could resist the forces generated during the tests without any deformation. The material generally used for this purpose is stainless steel. The fixture should be able to properly secure the test specimen.
- Force application system and the test frame- the test frame was rigid so as to not produce any movements while the application of the load. The force application system was designed such that the desired load could be applied in a controlled manner.
- Force and displacement sensor- the normal force applied was measured by the force sensor in newton. A tangential force sensor was also present to measure the tangential force on the specimen. The forces measured were measured as a function of time. The displacement sensor measured the distance traversed by the stylus in millimetres.

- Optical measurement- an instrumented travelling microscope was present to observe the scratches accurately and calculate the length of the scratch.
- Data acquisition and recording- the applied force as measured by the force sensor was recorded and correlated with the displacement of the stylus against time. The optical images of the scratches had to be clear enough to point out the force where the coating starts to peel.
- Acoustic emission system- the acoustic system was to help know the exact value of the critical load where the coating failed as sometimes the optical system cannot detect minute scratches.

II. Test Specimen

- The test specimen was a cuboid specimen of dimensions 30mm x 10mm x 3mm.
- Specimen 8 electroplated at 5 Adm^{-2} was tested for coating adhesion by the scratch testing method. From the scotch tape test it was evident that lower the plating current density, higher the adhesion strength. Hence, specimen 4 would have given the maximum adhesion strength but lowering the current density also increased the surface roughness and it is not possible to conduct scratch tests on rough surfaces. Hence, specimen 8 was chosen for scratch test as it had the maximum allowable surface roughness value (3-3.5 µm as suggested by the machine operator).

III. Procedure

- The specimen was cleaned, dried and properly secured on the specimen stage.
- The alignment and level of the specimen was checked and it was ensured that the stylus was perpendicular to the coated surface.
- The area of testing was selected and the stylus was positioned just over that area at least 2 mm away.
- The first test was the constant load test at 2N. This was done to check the effects of the load on the coating. Hence, the loading magnitude was selected to be small. The stylus was lowered to contact the specimen and the load was applied for 10 seconds. The stylus was then lifted and the coating checked for any sort of damage. Since there was no damage the progressive load test was conducted.
- The stylus was again lowered to contact the specimen and the minimum load (2N) was applied.
- The horizontal displacement, load progression and data recording were also initiated at the same time.
- The motion was stopped when the maximum load value (25N) was reached. The test took a time of 62.5 seconds.

- The stylus was then unloaded, the data checked and the damage assessed. The entire procedure must be repeated if the readings are not clear.
- In case more than one scratch needs to made, then the consecutive scratches should be made at a distance of at least 1 mm away from each other.
- The scratch was then assessed by the optical microscope and the scratch length was found out. The total distance traversed by the stylus was 5 mm and the scratch length was 2 mm.
- The tangential force was monitored and changes in the acoustic emission signal were also checked.
- The tangential force and the acoustic emission only act as supplementary signals for assessing the scratch damage that too if calibrated perfectly. The most reliable method for checking the damage is with the help of a microscope.
- The reflected light microscope was used to find out the load at which the coating started to peel off (critical load).

After the scratch was properly assessed, the data read and interpreted, the critical load value was found and hence, the adhesion strength was known. Since this is a quantitative analysis, there is no chart or pictorial representation to compare the result.

5.4 Conclusion

This chapter explained in detail the adhesion testing methods undertaken. There were two methods to conduct the scotch tape test; however, only method B was chosen as method A is not suitable for coating with thickness greater than 125 microns. The scotch tape test was conducted on three specimens namely specimen 1 (pre-treated specimen plated at 20 Adm^{-2}), specimen 2 (untreated specimen plated at 20 Adm^{-2}) and specimen 3 (untreated specimen plated at 1 Adm^{-2}). The results showed that pre-treatment was not as much a determining factor as current density to calculate coating adhesion. Since tape test is a qualitative test, a more accurate value of adhesion was required. This could be achieved by the shockwave test or the scratch test. The shockwave test being complicated and difficult to conduct, was not used and hence scratch testing was performed. A specimen electroplated at the optimum current density was tested for coating adhesion by the scratch test method. This method is a slightly more complicated method than the scotch tape test but gives the exact value of adhesion. After conducting the experiment, the scratch produced was carefully assessed by an optical microscope and the value of the critical load was found out. The results of the adhesion tests are presented in the next chapter.

Chapter 6

Results and Discussions

6.1 Introduction

In this chapter the results of all the experiments conducted have been shown serially. Firstly, the Scotch tape test results have been shown for three specimens. Based on the comparison chart provided by ASTM (shown in chapter 4), it can be clearly seen that specimens 1 and 2 can be designated as 0A and 1A respectively whereas specimen 3 can be designated as 5A. Secondly, ten more specimens have been plated and the surface roughness value of the coating of each specimen is computed to understand the relation between the plating current density and surface roughness. Thirdly, an attempt has been made to find out the average particle size of the deposited coating under various current densities. Fourthly, a specimen with an acceptable value of surface roughness has been tested by the scratch testing method to find out the critical load that the coating could withstand without failure. Finally, a finite element model of the scratch testing method has been made and analyzed.

6.2 The Scotch Tape test

The results of the scotch tape test are shown below in Figure 6.1 for the three specimens.

(a)

(b)

(c)

Figure 6.1. Scotch tape test results (a) specimen 1; (b) specimen 2; (c) specimen 3

Table 6.1 Scotch tape test results

Specimen Description	Adhesion Strength Designation
Specimen 1- pre-treated specimen plated at 20 Adm^{-2}	0A
Specimen 2- untreated specimen plated at 20 Adm^{-2}	1A
Specimen 3- untreated specimen plated at 1 Adm^{-2}	5A

The adhesion strength designation of the scotch tape test results are shown in Table 6.1. The results show that even though specimen 1 was pre-treated, still it did not have a satisfactory value for coating adhesion and the same applies to specimen 2 as well although it was not pre-treated. This shows that pre-treatment is not a determining step for coating adhesion. However, specimen 3 showed good adhesion (5A) in spite of not being pre-treated as it was electroplated at a much lower current density. The current densities for specimens 1 and 2 were 20 Adm^{-2} and that for specimen 3 was 1 Adm^{-2}. This proves that current density plays an important role in determining the coating adhesion.

6.3 Surface Roughness

To check the impact of current density on the surface roughness of the deposited coating, ten specimens of dimensions 30 mm x 10 mm x 3 mm were electroplated in varying current densities as described in chapter 4. The values of the surface roughness were found out with the help of a Talysurf Surtronic 3+ profilometer manufactured by Taylor Hobson, U.K. as shown in Figure 6.2. The result is shown in Table 6.2.

Figure 6.2. Talysurf Profilometer

Table 6.2 Variation of surface roughness with current density

Specimen No.	Current Density (Adm^{-2})	Surface Roughness (μm)
4	1	4.8
5	2	4.4
6	3	4.0
7	4	3.8
8	5	3.5
9	6	3.1
10	7	2.65
11	8	2.2
12	9	2.19
13	10	2.14

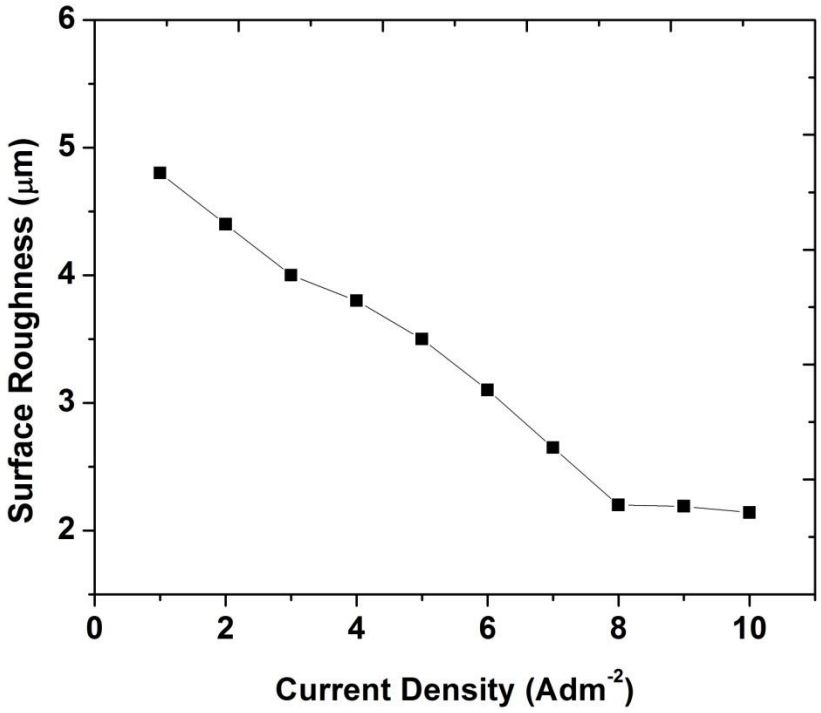


Figure 6.3. Variation of surface roughness with current density

Figure 6.3 shows the relation of surface roughness with current density. From the above table and graph it is clearly visible that the value of surface roughness decreases as we increase the current density. This is due to the fact that on increasing the current density the particle size decreases. Hence, to get a smoother coating, the current density should be increased. But this can reduce the coating adhesion as seen from

the scotch tape test. Thus, to get the benefit of both, an optimum current density should be chosen to give a decently smooth coating as well as a good value for coating adhesion.

6.4 Particle size determination

Since surface roughness depends largely on the particle size, hence, the effect of change in current density on the particle size being deposited was also studied with the help of a scanning electron microscope (SEM) JEOL - JSM-6480LV manufactured by the European Virtual Institute for Speciation Analysis (EVISA) shown in Figure 6.4 The SEM images of the ten specimens are shown in Figure 6.5.

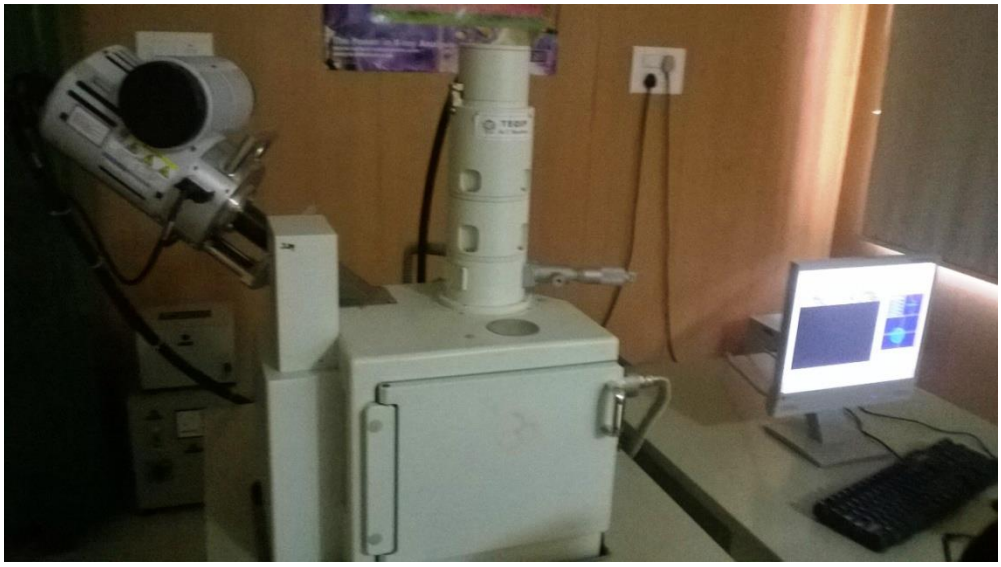
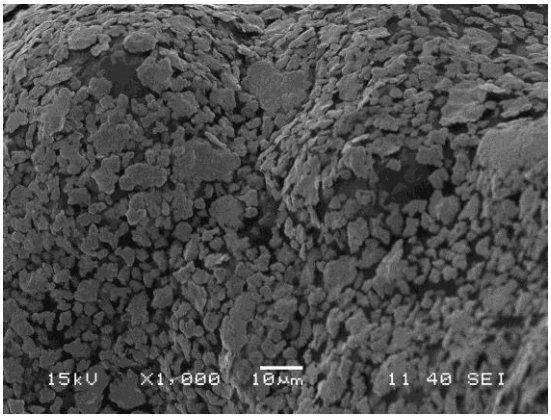
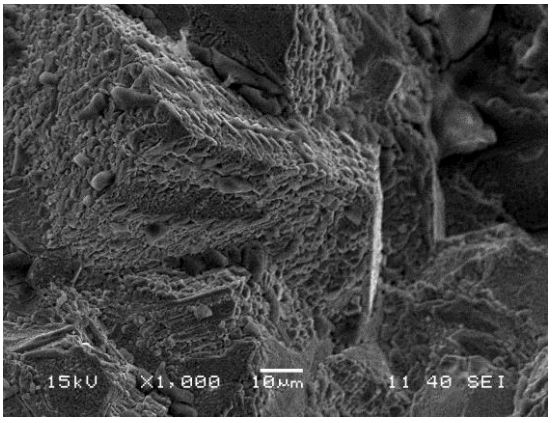


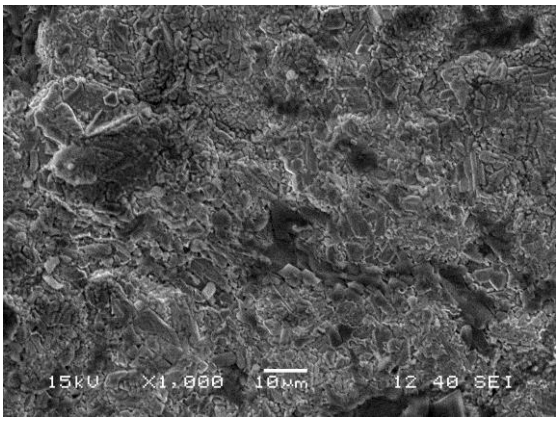
Figure 6.4. Scanning Electron Microscope used to check the particle size.



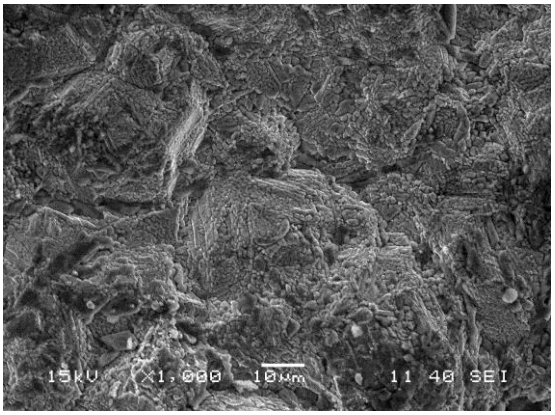
(a) Specimen 4



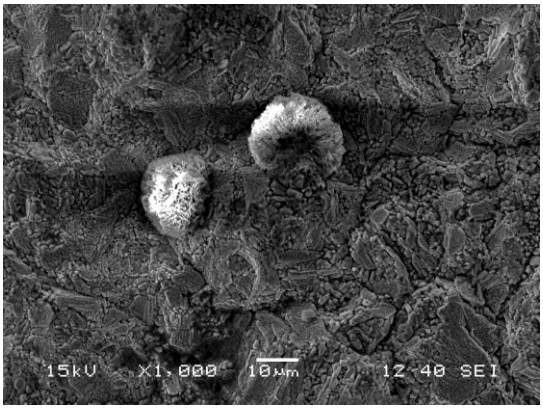
(b) Specimen 5



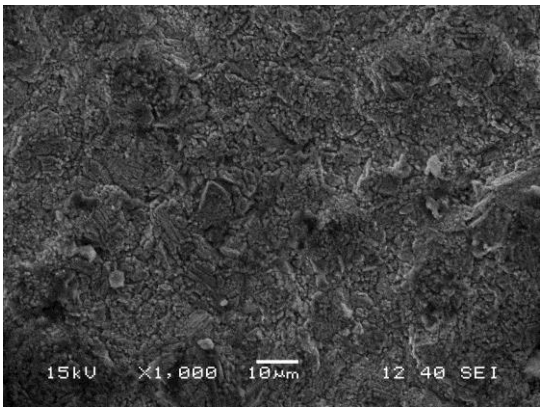
(c) Specimen 6



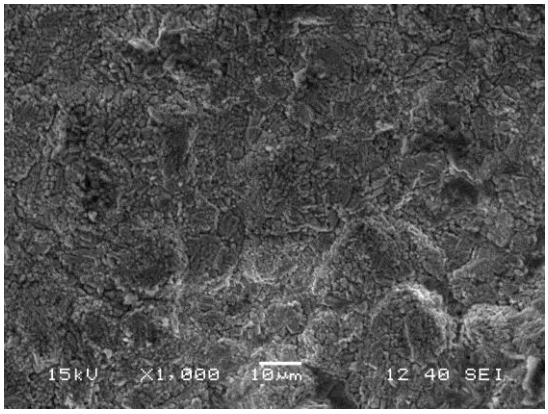
(d) Specimen 7



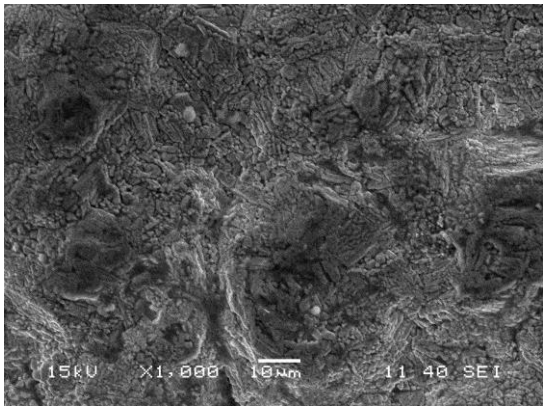
(e) Specimen 8



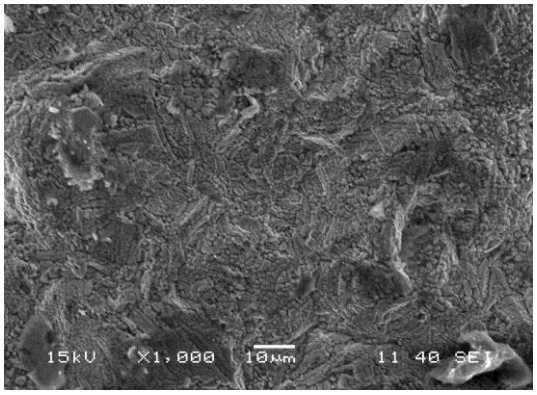
(f) Specimen 9



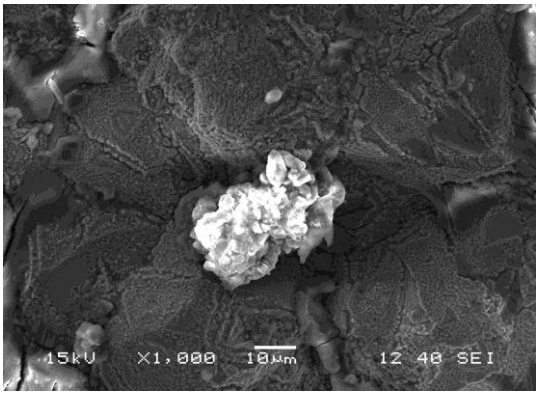
(g) Specimen 10



(h) Specimen 11



(i) Specimen 12



(j) Specimen 13

Figure 6.5. SEM images of the electroplated specimens at different current densities

Table 6.3 Avg. particle sizes of the ten specimens

Specimen No.	Current Density (Adm^{-2})	Avg. Particle size (microns)
4	1	5.5
5	2	5
6	3	4
7	4	3.5
8	5	3.3
9	6	3.2
10	7	2.5
11	8	2.1
12	9	1.5
13	10	1

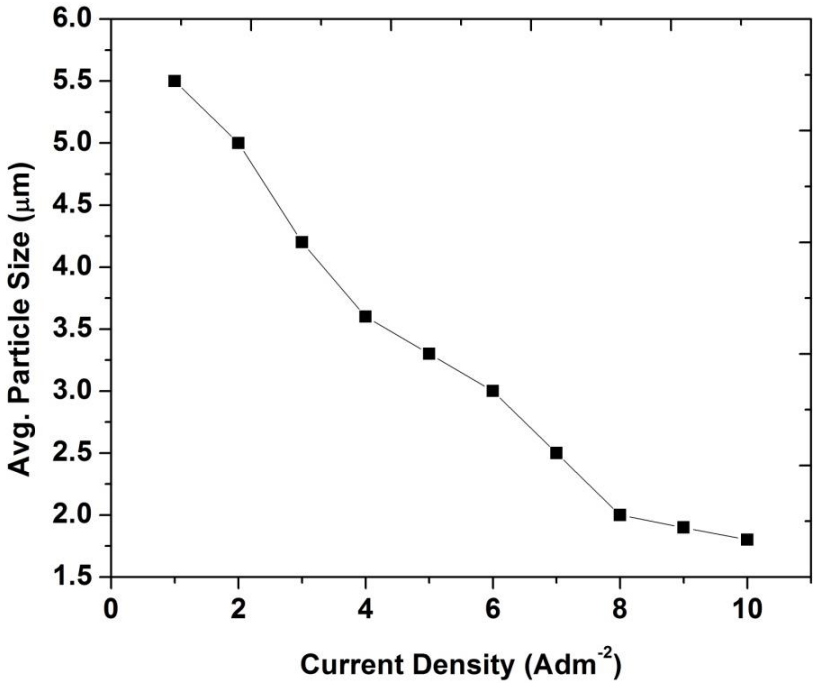


Figure 6.6. Variation of particle size with current density

The average sizes of the particles were calculated and plotted against the current density as shown in Figure 6.6. The plot shows that as the current density is increased, the deposited particles' sizes decrease. Increase in current density results in a higher

nucleation rate which leads to grain refinement. Hence, increase in current density reduces the deposited particle size.

The average coating thickness of the ten specimens was found out with the help of an optical microscope Axio Scope 332700043 manufactured by Carl Zeiss, Germany, shown in Figure 6.7. Table 6.4 shows the average coating thickness along with the plating time and current density. The coating thicknesses of all the specimens lie between 300-350 microns.

Figure 6.7. Optical microscope used for finding the coating thickness

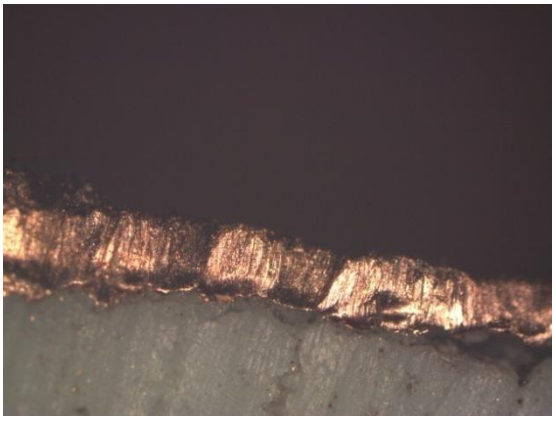
Table 6.4. Average coating thickness of the ten specimens

Specimen No.	**Current Density (Adm^{-2})**	**Time (mins)**	**Coating Thickness (μm)**
4	1	63	309
5	2	59	317
6	3	54	343
7	4	48	305
8	5	45	315
9	6	38	335
10	7	30	327
11	8	23	310
12	9	17	330
13	10	11	348

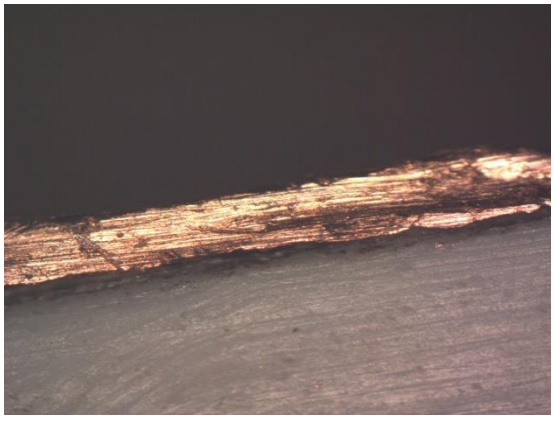
From Table 6.4 it can be concluded that to obtain a coating of a particular thickness, if a lower value of current density is used then the plating time required is high and if

the current density is higher then the plating time required is less. This is because on increasing the current density the potential difference between the electrodes increases. Increase in potential difference means the workpiece (cathode) is now at a higher negative potential than before which results in greater attraction of cations and hence more copper ions are deposited on the workpiece, thus, reducing the coating time.

The coating specimen interface for two samples is shown in Figure 6.8.



Specimen 8



Specimen 11

Figure 6.8. Coating substrate interfaces of two specimens

6.5 Scratch Adhesion Testing

Specimen 8 was selected as its surface roughness value was not very high and the adhesion strength was expected to be decent enough. The results of the test are shown in Table 6.5.

Table 6.5. Scratch Adhesion Testing results

Time (sec)	F_x (N)	F_z (N)	AE (v)	Z (mm)	Y (mm)	X (mm)	F_f (N)	COF
0	-0.51193	-1.99036	-0.00192	0	0	-3.076	0.511932	0.257206
1	-1.03867	-2.13959	-0.00143	0.001	-0.0105	-3.076	1.038666	0.485451
2	-1.30142	-2.56027	0.000122	0.003	-0.02325	-3.076	1.301422	0.508314
3	-1.49002	-2.97638	0.000153	0.0045	-0.0365	-3.076	1.490021	0.500615
4	-1.59973	-3.3429	-0.00205	0.0055	-0.0495	-3.076	1.599731	0.478547
5	-1.67069	-3.67722	0.000092	0.0065	-0.0625	-3.076	1.670685	0.454334
6	-1.71082	-4.0448	0.001282	0.0075	-0.07525	-3.076	1.710815	0.422967
7	-1.7247	-4.38782	-0.0054	0.009	-0.0885	-3.076	1.724701	0.393066
8	-1.72974	-4.71314	-0.00079	0.0105	-0.1015	-3.076	1.729736	0.367003
9	-1.79672	-5.09354	0.001892	0.0125	-0.1145	-3.076	1.796722	0.352746
10	-1.87485	-5.42954	-0.00272	0.0145	-0.12725	-3.076	1.874847	0.345305
11	-1.98074	-5.80063	-0.00192	0.0165	-0.1405	-3.076	1.980743	0.34147

12	-2.10739	-6.15906	-0.00214	0.0185	-0.1535	-3.076	2.107391	0.342161
13	-2.23862	-6.55045	-0.00348	0.0205	-0.1665	-3.076	2.238617	0.34175
14	-2.32101	-6.89758	-0.00229	0.023	-0.17925	-3.076	2.321014	0.336497
15	-2.42416	-7.25037	-0.00195	0.025	-0.1925	-3.076	2.424164	0.334351
16	-2.60346	-7.60132	-0.00116	0.0275	-0.2055	-3.076	2.603455	0.3425
17	-2.78229	-7.95136	-0.00018	0.03	-0.2185	-3.076	2.782288	0.349914
18	-2.96799	-8.35571	-0.00366	0.0325	-0.2315	-3.076	2.967987	0.355205
19	-3.19367	-8.69537	-0.00089	0.035	-0.2445	-3.076	3.193665	0.367283
20	-3.40042	-9.06647	-0.00394	0.037	-0.25725	-3.076	3.400421	0.375055
21	-3.75626	-9.49661	-0.0011	0.0395	-0.27025	-3.076	3.756256	0.395536
22	-4.09195	-9.85413	-0.00284	0.0415	-0.28325	-3.076	4.091949	0.415252
23	-4.36844	-10.2382	-0.00183	0.044	-0.2965	-3.076	4.368439	0.426681
24	-4.6048	-10.5748	-0.00302	0.0455	-0.30925	-3.076	4.604797	0.43545
25	-4.81003	-10.9573	-0.00116	0.048	-0.3225	-3.076	4.810028	0.438978
26	-4.98489	-11.2918	-0.00177	0.05	-0.33525	-3.076	4.984894	0.441461
27	-5.20645	-11.6879	-0.00595	0.052	-0.34825	-3.076	5.206451	0.445455
28	-5.53116	-12.0143	-0.004	0.0545	-0.3615	-3.076	5.531158	0.460381
29	-6.01379	-12.4533	-0.00162	0.0565	-0.37425	-3.076	6.013794	0.482907
30	-6.55945	-12.7951	0.00310	0.058	-0.38725	-3.076	6.559448	0.512653
31	-7.02728	-13.1946	0.000061	0.06	-0.40025	-3.076	7.027283	0.532589
32	-7.44965	-13.5541	-0.00302	0.062	-0.41325	-3.076	7.449646	0.549624
33	-7.82562	-13.9284	-0.00253	0.064	-0.426	-3.076	7.825623	0.561848
34	-8.15918	-14.2657	-0.0007	0.066	-0.43925	-3.076	8.15918	0.571942
35	-8.414	-14.6584	-0.00159	0.068	-0.45225	-3.076	8.414001	0.574007
36	-8.62503	-15.0113	-0.00211	0.0695	-0.46525	-3.076	8.625031	0.57457
37	-8.84323	-15.3989	-0.00101	0.0715	-0.47825	-3.076	8.843231	0.574278
38	-9.04526	-15.7565	-0.00266	0.073	-0.49125	-3.076	9.045258	0.574064
39	-9.21204	-16.1201	-0.00244	0.075	-0.504	-3.076	9.212036	0.571461
40	-9.36997	-16.4879	-0.00272	0.077	-0.517	-3.076	9.369965	0.568294
41	-9.48105	-16.8362	0.000946	0.0785	-0.53	-3.076	9.481049	0.563133
42	-9.59152	-17.2227	0.002106	0.081	-0.543	-3.076	9.591522	0.55691
43	-9.66873	-17.5772	-0.00308	0.083	-0.556	-3.076	9.668732	0.550072
44	-9.72611	-17.9279	-0.0015	0.085	-0.56925	-3.076	9.726105	0.542514
45	-9.80133	-18.2787	-0.00043	0.0875	-0.58225	-3.076	9.801331	0.536217
46	-9.982	-18.6206	-0.00714	0.09	-0.595	-3.076	9.981995	0.536072
47	-10.3355	-19.0405	-0.00079	0.092	-0.608	-3.076	10.33554	0.542818
48	-10.6731	-19.3782	-0.00339	0.094	-0.62125	-3.076	10.67307	0.550777
49	-10.9303	-19.7647	-0.00482	0.0965	-0.634	-3.076	10.93033	0.553022
50	-11.1334	-20.1187	-0.00403	0.0985	-0.647	-3.076	11.13342	0.553386
51	-11.4195	-20.5205	-0.00192	0.101	-0.65975	-3.076	11.41953	0.556494
52	-11.7264	-20.9003	0.000092	0.103	-0.673	-3.076	11.72638	0.561064
53	-11.9051	-21.2442	-0.00528	0.1055	-0.68575	-3.076	11.90506	0.560391
54	-12.1115	-21.6054	0.00058	0.1075	-0.69875	-3.076	12.11151	0.560579
55	-12.2733	-21.9411	-0.00235	0.1095	-0.71175	-3.076	12.27325	0.559374
56	-12.43	-22.3358	0.000427	0.112	-0.725	-3.076	12.42996	0.556504
57	-12.5418	-22.6598	-0.00241	0.1145	-0.73775	-3.076	12.54181	0.553484
58	-12.717	-23.0295	-0.00153	0.117	-0.751	-3.076	12.71698	0.552204

59	-12.8183	-23.4047	-0.00189	0.1195	-0.76375	-3.076	12.8183	0.547681
60	-12.9521	-23.7703	-0.0043	0.1225	-0.77675	-3.076	12.95212	0.544887
61	-13.0264	-24.1116	-0.00391	0.1255	-0.78975	-3.076	13.02643	0.540255
62	-12.9164	-24.4725	-0.00015	0.1285	-0.7995	-3.076	12.91641	0.527793
62.86	-12.6889	-24.789	-0.00293	0.1305	-0.7995	-3.076	12.6889	0.511877

The notations used in Table 6.3 are as follows:

F_Z - Applied force in newton

F_X - Shear force generated due to F_Z in newton

AE - Acoustic Emission signal in volts

Z - Depth of the scratch in mm

Y - Length of the scratch in mm

X - Width of the scratch in mm

F_f - Frictional force in newton

COF - Coefficient of Friction (F_Z/F_X)

The negative signs preceding the force readings indicate a compression force.

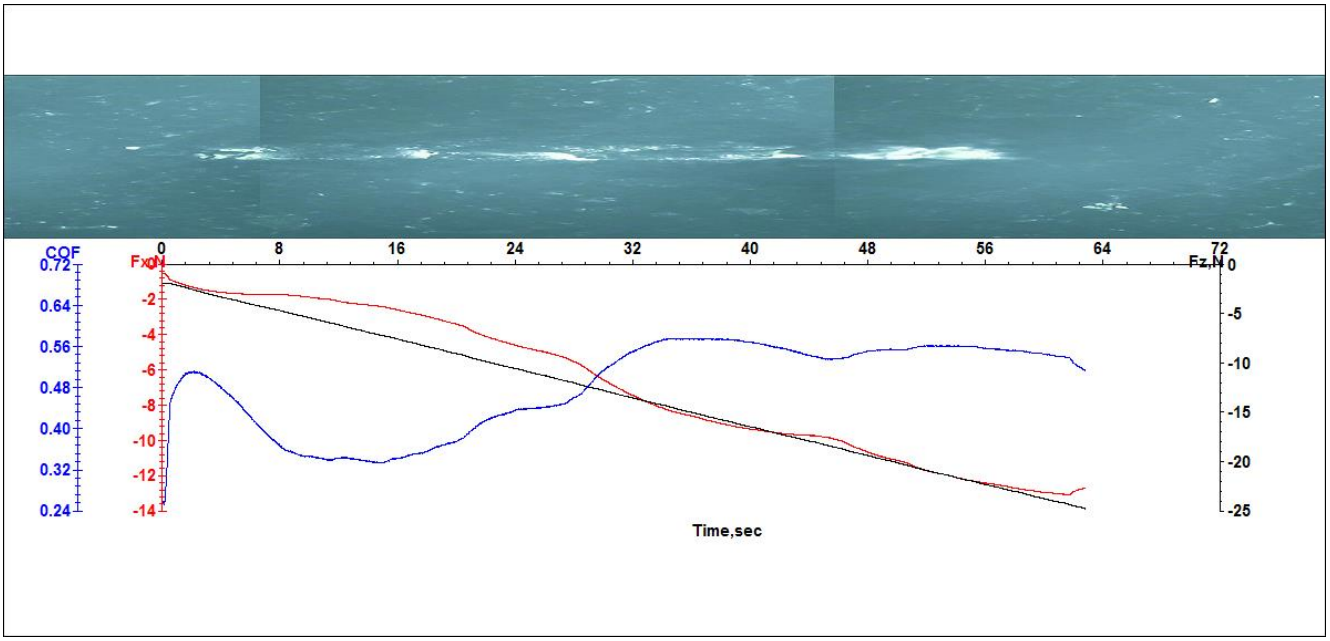


Figure 6.9. Microscopic image of the generated scratch

The generated scratch and the force readings are shown in Figure 6.9. The scratch starts in the 28th second, i.e. when the load is -12.0143 N. Some scratch is visible in the starting but that is mainly due to the presence of external impurities on the specimen. Hence, the scratch is discontinuous in those parts. Therefore, the value of critical load was found out to be 12.0143 N i.e. the deposited coating can withstand a force of upto 12.0143 N without being damaged.

6.6 Finite Element Modelling

A finite element model was made and analyzed in ANSYS R15. The analysis was done to check the maximum stress and strain concentration zones [42-44]. The following assumptions and boundary conditions were considered for the analysis:

Assumptions

- The materials are isotropic and homogeneous.
- The diamond indenter is assumed to have sliding friction.
- The model is developed for adiabatic process only.

Boundary Conditions

The boundary conditions considered for the analysis are mentioned below and shown in Figure 6.10.

- The ABS workpiece is fixed at all sides.
- The contact type between copper and ABS is treated as bonded.
- The contact type between copper and diamond is treated as rough.
- The diamond stylus is given a velocity of 5 mm/min along the surface of the workpiece.
- The diamond stylus is given a progressive compressive load of 2-25 N in 62.86 seconds perpendicular to the surface of the workpiece.

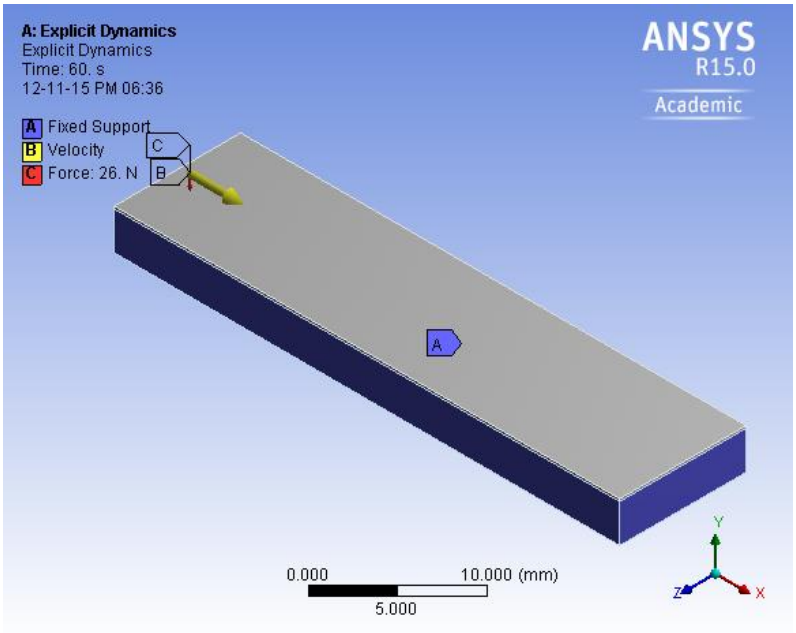
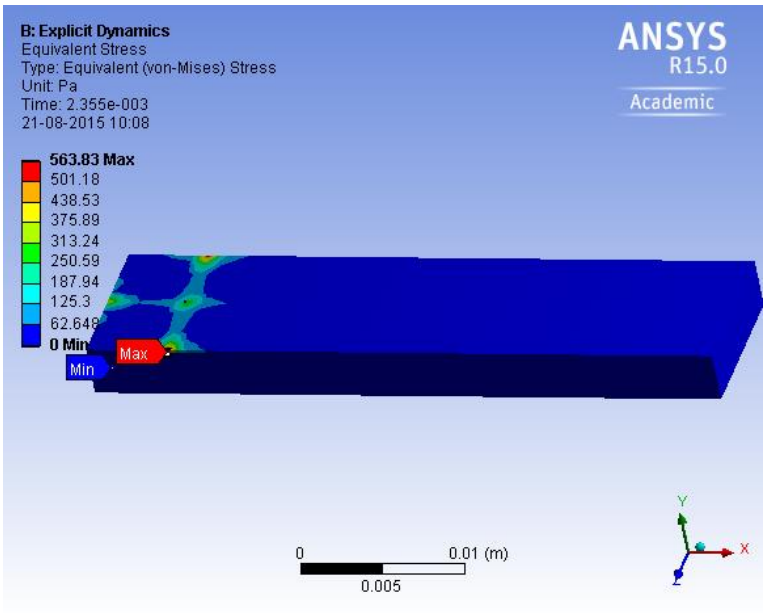
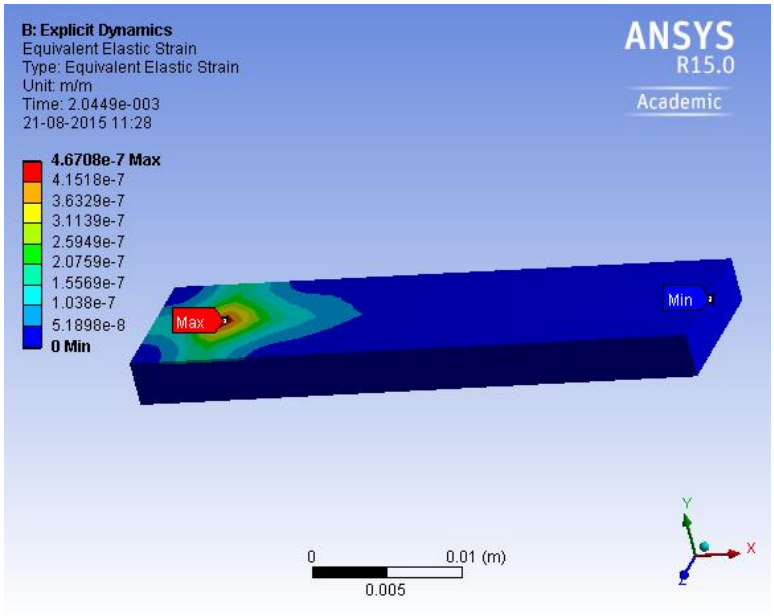


Figure 6.10. Boundary Conditions of the analysis



(a)



(b)

Figure 6.11. Finite Element Modelling showing (a) stress concentration zones; (b) strain concentration zones

From the FEM analysis shown in Figure 6.11 it is observed that the maximum stress occurs at the coating-substrate interface which points to adhesive failure. If the maximum stress had occurred in the central part of the coating then the failure would have been assumed as cohesive. A cohesive failure suggests the degradation of the coating itself which means the entire coating can get damaged all at once (as cohesive failure usually generates propagating cracks) whereas an adhesive failure means only the affected area will sustain the damage leaving the rest of the coating intact. The

analysis also shows that the maximum deformation occurred in the path of the indenter resulting in the scratch.

6.7 Conclusion

This chapter points out that when electroplating a non-conductor, pre-treatment processes prior to making the specimen conductive is not necessary and these processes do not play an important role in the determination of the adhesion strength coating. However, the electroplating current density can change the adhesion strength and it was found out that on increasing the current density the adhesion strength decreased and so did the surface roughness and particle size. On conducting the scratch adhesion test on the specimen the critical load was found out and a finite element analysis showed the stress and strain concentration zones.

Chapter 7

Conclusion

7.1 Introduction

In this research work, an alternate method has been suggested for preserving artefacts by making prototypes via RP routes which is faster, easier and cost effective. An original artefact was scanned with the help of a 3D scanner for manufacturing the specimens. The specimens were fabricated using FDM technology (Chapter 3). Three specimens have been electroplated in different conditions and their adhesion strength has been checked by the scotch tape test method. Based on those results, more specimens were plated in varying current densities and the surface roughness and particle size of the deposited coating have been analyzed (Chapter 4). After the scotch tape test, scratch adhesion test was conducted on a specimen to find the coating adhesion in a qualitative manner. This experiment gave us the critical load value (Chapter 5). Finally, a finite element model was made to understand the stress and strain concentration zones. The outcomes are shown in the following section in detail.

7.2 Summary of Results

In chapter 3, the specimens were manufactured using a RP technique known as FDM. This method has many advantages over others such as it is cost effective, takes less time and the wastage is minimal. The fabricated specimens were electroplated at different current densities as explained in Chapter 4. The necessity of the pre-treatment processes was also examined and it was found out that the current density was a much important factor for deciding the coating adhesion. It was also seen that as we increased the electroplating current density, the surface roughness of the coating decreased and so did the particle size. In chapter 5, the results of the adhesion tests have been described. It can be confirmed from those tests that increasing the current density has a negative impact on the adhesion strength of the coating. From the scratch test, it was found out that an ABS specimen electroplated at 5 Adm^{-2} could resist a load of 12.0143 N before its coating starts to peel off. The value of 12.0143 N is the critical load that the coating can withstand without peeling.

7.3 Major contribution to research work

Through an exhaustive literature survey and detailed experimental work, the following contributions have been made by this study:

- A new method for preserving artefacts has been presented which also brings to light the applications of ABS plastic in place of plated metal parts.
- It is proven that the need for pre-treating a non-conducting specimen prior to making it conductive is not necessary, thus saving time for practicing engineers.

- The relation of the current density with the adhesion strength, surface roughness and particle size has been examined. Thus, from now on the plating parameters can be optimized from the beginning of the experiment depending upon the desired result.
- The adhesion strength of a copper coating on an ABS specimen electroplated at a particular parameter setting has been given, thus providing a general idea about copper coatings.

7.4 Limitations of the study

In spite of providing an in-depth knowledge about electroplating of copper on ABS, there are certain issues that have not been considered in this study which can be treated as its limitations. They are:

- Power failure in an ongoing electroplating process has been ignored.
- The effect of slight agitations in the electrolyte solution has also not been considered.

7.5 Future Work

This research work provides a wide range of activities of copper plating on ABS to be explored by future investigators. Some of the recommendations are:

- Assessing the change in hardness of the specimen due to the deposited copper.
- Calculating the wear rate of the coating under different process parameters.
- Checking the corrosion resistance of the coating.

BIBLIOGRAPHY

[1] Noorani R. (2006) *Rapid Prototyping-Principles and Application*, 1st ed., New Jersey, USA.

[2] Lee, J. and Huang, A. (2013) 'Fatigue analysis of FDM materials', *Rapid Prototyping Journal*, Vol. 19 No. 4, pp.291–299.

[3] Galantucci, L. M., Lavecchia, F. and Percoco, G. (2009) 'Experimental study aiming to enhance the surface finish of fused deposition modeled parts', *CIRP Annals - Manufacturing Technology*, Vol. 58 No. 1, pp.189–192.

[4] Vasudevarao, B., Natarajan, D. P. and Henderson, M. (2000) 'Sensitivity of RP surface finish to process parameter variation', Proceedings of the Solid Freeform Fabrication Symposium, The University of Texas, Austin, pp. 252-258.

[5] Leibig, V. J. (1861) 'Improvement in electroplating with copper and other metals the silvered surfaces of mirrors and other articles for protecting the same', US Patent 33721.

[6] Walker, B. F. and Cedarhurst, N. Y. (1940) 'Metal coated plastic material and method of producing the same', US Patent 2214616.

[7] Rode, E.-D. (1978) 'Method of regulating cathode current density in an electroplating process', US Patent 4100036.

[8] Griehl, S., Muller, T. and Winkler, R. (2003) 'Thick metallization-layers on polymers through vacuum-technology', *Surface and Coatings Technology*, Vol. 170, pp.24–26.

[9] De Bruyn, K., Van Stappen, M., De Deurwaerder, H., Rouxhet, L. and Celis, J. P. (2003) 'Study of pretreatment methods for vacuum metallization of plastics', *Surface and Coatings Technology*, Vol. 163-164, pp.710–715.

[10] Narcus, H., Electroplat, M., Wiley, J. and Smith, P. E. D. (1979) 'Bright electroless plating process and plated articles produced thereby', US Patent 4169171.

[11] Krulik, G. A. (1982) 'Tin-Palladium Catalysts for Electroless Plating', *Platinum Metals Review*, Vol. 26 No. 2, pp.58–64.

[12] Yen, P. (1995) 'Improved ABS plastic activating treatment for electroless copper plating', *Polymer*, Vol. 36 No. 17, pp.3399–3400.

[13] Kruse, A., Kruger, G., Baalmann, A. and Hennemann, O.-D. (1995), “Surface pretreatment of plastics for adhesive bonding”, *Journal of Adhesion Science and Technology*, Vol. 9 No. 17, pp.1611-1621.

[14] Cheng, D. H., Xu, W. Y., Zhang, Z. Y. and Yiao, Z. H. (1997) ‘Electroless copper plating using hypophosphite as reducing agent’, *Metal Finishing*, Vol. 95 No. 1, pp.34–37.

[15] Ono, S., Naitoh, K. and Osaka, T. (1999) ‘Initial propagation stage of direct copper plating on non-conducting substrates’, *ElectrochimicaActa*, Vol. 44 No. 21, pp.3697–3705.

[16] Teixeira, L. A. C. and Santini, M. C. (2005) ‘Surface conditioning of ABS for metallization without the use of chromium baths’, *Journal of Materials Processing Technology*, Vol. 170 No. 1, pp.37–41.

[17] Gui-xiang, W., Ning, L., Hui-li, H. and Yuan-chun, Y. (2006) ‘Process of direct copper plating on ABS plastics’, *Applied Surface Science*, Vol. 253 No. 2, pp.480–484.

[18] Yfantis, D. K., Kakos, S. I., Lamprakopoulos, S., Depountis, S. and Yfantis, C., Schmeisser, D. (2006) ‘New environment friendly methods and materials in surface treatment’, Proceedings of the 2006 IASME/WSEAS International Conference on Energy & Environmental Systems, Chalkida, Greece, pp.11-14.

[19] Tang, X., Cao, M., Bi, C., Yan, L. and Zhang, B. (2008)‘Research on a new surface activation process for electroless plating on ABS plastic’, *Materials Letters*, Vol. 62 No. 6, pp.1089–1091.

[20] Inagaki, N. and Kimura, H. (2008) ‘Electroless copper plating on acrylonitrile butadiene styrene material surfaces without chromic acid etching and a palladium catalyst’, *Journal of Applied Polymer Science* Vol. 111 No. 2, pp.1034-1044.

[21] Li, D., Goodwin, K. and Yang, C.-L. (2008) ‘Electroless copper deposition on aluminum-seeded ABS plastics’, *Journal of Materials Science*, Vol. 43, pp.7121–7131.

[22] Ng C. S., Mak, C. L. and Wong, Y. W. (2008) ‘Wet pre-treatment of poly(butylene) terephthalate-poly(ethylene) terephthalate blend and subsequent metallization by electroplating’, *physica status solidi*, Vol. 5, pp.3535-3540.

[23] Dechasit, P. and Trakarnpruk, W. (2011) 'Ni electroless plating of ABS polymer by palladium and tin-free process', *Journal of Metals, Materials and Minerals*, Vol. 21 No. 2, pp.19–27.

[24] Bazzaoui, M., Martins, J. I., Bazzaoui, E. A., Albourine, A., Wang, R. and Hong, P.-D. (2013) 'A simple method for acrylonitrile butadiene styrene metallization', *Surface and Coatings Technology*, Vol. 224, pp.71–76.

[25] Shu, Z. and Wang, X. (2012) 'Environment-friendly Pd free surface activation technics for ABS surface', *Applied Surface Science*, Vol. 258 No. 14, pp.5328–5331.

[26] Ma, Q., Zhao, W., Li, X., Li, L. & Wang, Z. (2013) 'Study of an environment-friendly surface pretreatment of ABS-polycarbonate surface for adhesion improvement', *International Journal of Adhesion and Adhesives*, Vol. 44, pp.243–249.

[27] Yu, L. Yu., Shen, H. M. and Xu, Z. L. (2009) 'PVDF–TiO2 Composite Hollow Fiber Ultrafiltration Membranes Prepared by TiO2 Sol–Gel Method and Blending Method', *Journal of Applied Physics*, Vol. 113, pp.1763–1772.

[28] Luo, L. M., Lu, Z. L., Huang, X. M., Tan, X. Y., Ding, X. Y., Cheng, J. G. and Wu, Y. C. (2014) 'Electroless copper plating on PC engineering plastic with a novel palladium-free surface activation process', *Surface and Coatings Technology*, Vol. 251, pp.69–73.

[29] Equbal, A. and Sood, A. K. (2015) 'Investigations on metallization in FDM build ABS part using electroless deposition method', *Journal of Manufacturing Processes*, Vol. 19, pp.22–31.

[30] Gangadhar, A., Shunmugam, M. S. and Philip, P. K. (1991) 'Surface modification in electrodischarge processing with a powder compact tool electrode', *Wear*, Vol. 143 No. 1, pp.45–55.

[31] Wang, Z. L., Fang, Y., Wu, P. N., Zhao, W. S. and Cheng, K. (2002) 'Surface modification process by electrical discharge machining with a Ti powder green compact electrode', *Journal of Materials Processing Technology*, Vol. 129No. 1, pp.139–142.

[32] Ho, S. K., Aspinwall, D. K. and Voice, W. (2007) 'Use of powder metallurgy (PM) compacted electrodes for electrical discharge surface alloying/modification of Ti–6Al–4V alloy', *Journal of Materials Processing Technology*, Vol. 191 No. 1, pp.123–126.

[33] Hsu, C. Y., Chen, D. Y., Lai, M. Y. and Tzou, G. J. (2008) 'EDM electrode manufacturing using RP combining electroless plating with electroforming', *The International Journal of Advanced Manufacturing Technology*, Vol. 38 No. 9, pp.915–924.

[34] Monzón, M., Benítez, A. N., Marrero, M. D., Hernández, N., Hernández, P. and Aisa, J. (2008)'Validation of electrical discharge machining electrodes made with rapid tooling technologies', *Journal of Materials Processing Technology*, Vol. 196 No. 1, pp.109–114.

[35] Hwang, Y.-L., Kuo, C.-L. and Hwang, S.-F. (2010) 'The coating of TiC layer on the surface of nickel by electric discharge coating (EDC) with a multi-layer electrode', *Journal of Materials Processing Technology*, Vol. 210 No. 4, pp.642–652.

[36] Chen, H.-J., Wu, K.-L. and Yan, B.-H. (2013) 'Dry Electrical Discharge Coating Process on Aluminum by Using Titanium Powder Compact Electrode', *Materials and Manufacturing Processes*, Vol. 28 No. 12, pp.1286–1293.

[37] Krishna, M. E. and Patowari, P. K. (2014) 'Parametric Study of Electric Discharge Coating Using Powder Metallurgical Green Compact Electrodes', *Materials and Manufacturing Processes*, Vol. 29 No. 9, pp.1131-1138.

[38] Mordechay,S. and Milan, P. (2005) *Modern Electroplating*, 5th ed., New Jersey, USA.

[39] Perry, A. J. (1983) 'Scratch adhesion testing of hard coatings', *Thin Solid Films*, Vol. 107 No. 2, pp.167–180.

[40] Steinmann, P. A., Tardy, Y. and Hintermann, H. E. (1987) 'Adhesion testing by the scratch test method: The influence of intrinsic and extrinsic parameters on the critical load', *Thin Solid Films*, Volume 154 No. 1, pp.333–349.

[41] Bull, S. J., Rickerby, D. S., Matthews, A., Leyland, A., Pace, A. R. and Valli, J. (1988) 'The use of scratch adhesion testing for the determination of interfacial adhesion: The importance of frictional drag', *Surface and Coatings Technology*, Vol. 36 No. 1, pp.503–517.

[42] Gonçalves, J. P., De Moura, M. F. S. and De Castro, P. M. S. (2002)'A three-dimensional finite element model for stress analysis of adhesive joints', *International Journal of Adhesion and Adhesives*, Vol. 22, pp.357–365.

[43] Bucaille, J. L., Felder, E. and Hochstetter, G. (2001) 'Mechanical analysis of the scratch test on elastic perfectly plastic materials with the three-dimensional finite element modelling', *Wear,* Vol. 249 No. 5, pp.422–432.

[44] Li, J. and Beres, W. (2006) 'Three-dimensional finite element modelling of the scratch test for a TiN coated titanium alloy substrate', *Wear*, Vol. 260, pp.1232–1242.

List of publications

International Journal (communicated)

[1] Mishra, S.B., Malik, R. and Mahapatra, S.S. 'Enhancement of Flexural Strength of FDM Build Parts using a Metaheuristic Approach', *Additive Manufacturing.*

International Conference

[1] Mishra, S.B., Malik, R. and Mahapatra, S.S. (2015) 'An Experimental Investigation on Flexural Strength of FDM Built Parts', Proceeding of the International Conference on Advances in Materials, Manufacturing and Applications, Trichy, India.